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EP 0 330 522 B1

Description

This invention relates to oleaginous compositions containing high molecular weight ashless dispersant and demulsifier additive having improved demulsibility. Such concentrates are useful in oleaginous compositions, including fuel and lubricating oil compositions.

The Sequence IID is one of the established ASTM tests which define the current standard of crankcase lubricants for gasoline engines (American Society for Testing and Materials Special Technical Publication 315H, Part 1; September 15, 1979). The test, designed to evaluate the rust-preventive properties of the lubricant, creates an environment conducive to rust formation, in part by retaining water vapor from combustion gases in the crankcase with the use of a condenser at the crankcase breather outlet.

A by-product of the wet IID environment is the presence of conditions that are very conducive to emulsion formation. Although emulsions would not necessarily be a matter of concern in themselves, the condenser tubes can become partially blocked with emulsion, leading to a pressure drop across the condenser and resultant pressure development in the crankcase. Engine manufacturers have become concerned that oils which develop emulsions may also tend in the field to plug PCV valves or other lines associated with the crankcase ventilation system, and to coat other internal engine surfaces such as the rocker covers, valve deck, etc. with emulsion. These concerns are particularly directed to internal combustion engines wherein fresh air purge of the crankcase is not employed. In such cases, the absence of fresh air purge can cause build-up of water in the crankcase vapors. In some engines, crankcase vapors are passed to an external separator intended to separate entrained liquids and vapors. The separated liquids are intended to continuously drain back into the crankcase, and the gases passing through the separator are intended to be combined with air and/or fuel (or mixtures thereof) for charging to the engine's cylinder for combustion. The presence of emulsion in the crankcase, and in the entrained vapors passing to the separator, causes plugging of, or at least a buildup in the effective pressure drop across, the separator, decreasing its efficiency. This, in severe cases, may result in an unintended increase in crankcase pressure beyond design limits, which, in turn, can cause oil seepage through crankcase seals, and other problems. In cold climates, and in short-trip or low-engine speed conditions, the above problems may become more pronounced.

Crankcase lubricants for internal combustion engines are required to suspend solids resulting, e.g., from the inevitable oxidation of the oils components during operation of the engine, to minimize both the degree of deposits (e.g., varnish) on engine components and the formation of sludge. Since modern engines operate at high temperatures, as a result of the decreased engine sizes and high power demands, modern crankcase lubricant formulations require the use of high levels of dispersancy (e.g., provided by use of high molecular weight dispersants or increased levels of lower molecular weight dispersants), and the use of other potent engine components, to minimize the adverse consequences on the engine of the oxidation of the lubricant during use.

Therefore, stricter limits on crankcase pressure have been suggested in the Sequence IID test, and it has become very important to prevent emulsion formation in modern lubricating oil formulations.

Unfortunately, the critical components that are necessary to maintain engine cleanliness and control deposit formation in modern lubricating oil formulations, many dispersants and multifunctional viscosity modifiers, can be highly potent emulsion formers.

A large variety of lubricating oil demulsifiers have been suggested heretofore.

US-A-3,509,052 discloses lubricating oil demulsifiers comprising certain alkylphenoxy poly(ethylene oxy) ethyl-mono- and diesters of phosphoric acid, polyoxyethylated amines, amides and quaternary salts, and polyoxyalkylene polyols and esters of such polyoxyalkylene polyols with lauric acid, stearic acid, succinic acid, and alkyl- or alkenyl-substituted succinic acids (up to 20 carbons in the alkyl or alkenyl group).

US-A-3,511,882 relates to crude oil petroleum demulsifiers prepared by adding a higher alkylene oxide, e.g., butylene oxide or propylene oxide, to a monohydric, dihydric or trihydric compound (e.g., propylene glycol). Thereafter ethylene oxide is added to the first adduct to form an oxyethylated adduct in which the proportion of primary hydroxyl groups to secondary hydroxyl groups is controlled. The oxyethylated adduct is then reacted with an epoxide of a polyphenol, preferably a diglycidyl ether of bis-phenol A. Demulsification is achieved by use of mixing of the demulsifying agents with the crude oil, emulsions in a ratio of about 1 part of the demulsifying agent to 2000 to 50,000 parts of the emulsion, and thereafter allowing the emulsion to remain in a relatively quiescent state during which separation of the oil and water occurs. It is disclosed that these demulsifiers may be used in combination with other demulsifying agents from classes such as petroleum sulfonate types, of which naphthenene sulfonic acid is an example, the modified fatty acid type, and the amine modified oxyalkylated phenol-formaldehyde type.

US-A-2,996,551 describes demulsifying agents for petroleum emulsions generally which include the reaction product of an aliphatic diepoxide with the adduct of propylene oxide and a polyol. No results of its use in combination with other lubricant additives are reported.

Crude oil demulsifiers have heretofore been used in the breaking of crude petroleum oil emulsions (e.g. in down well applications) which comprise adducts obtained by reacting diglycidyl ether of bis-phenol A with polypropylene glycol and the propoxylated derivatives thereof.

However, the environment in which demulsifiers are employed in the breaking of crude oil emulsions, and the manner in which such quiescent state for emulsion phase separation is permitted to occur, are distinct from the dynamic flow and shear environment in which crankcase lubricating oils are employed in internal combustion engines and are also to be contrasted with the variety of other lubricating oil additives which are employed in crankcase lubricating compositions, as discussed above. Principally among these, the effect of ashless dispersants in crankcase lubricating oils can be counteracted by demulsifiers.

The modern trend to the use of higher molecular-weight ashless dispersants in such formulations, and in additive concentrates therefor, has greatly complicated the search for more potent demulsifier additives. In addition, the frequent simultaneous use in such formulations and concentrates of high total base number metal detergents requires the demulsifier to be compatible with these compositions, that is, the demulsifier should not adversely affect these products' storage stability.

Heretofore, many lubricants and fuels have contained compounds known as friction modifiers (also termed "lubricity additives"), which act to reduce the friction of internal engine parts and thereby increase fuel economy. US-A-3,429,817 relates to the improvement of the lubricity and load carrying ability of a synthetic ester lubricating oil by addition of an ester formed by reacting about 2 moles of C₂ to C₅ glycol with about 1 mole of C₃₆ dicarboxylic acid dimer of a C₁₈ unsaturated fatty acid (e.g., linoleic acid or oleic acid). US-A-3,273,981 is directed to fuels and lubricating oil containing as lubricating additive a mixture of dimer acids and polyhydric alcohol partial esters. US-A-4,459,223 relates to lubricating oil friction reducing additives which are the reaction product of a dimer carboxylic acid (e.g., linoleic acid dimers) and a polyhydric alcohol having at least 3 hydroxyl groups. US-A-4,479,883 relates to lubricating oil compositions having a relatively low level of phosphorous and improved friction reducing properties by use of a mixture of a glycol or glycerol ester of a polycarboxylic acid (e.g., linoleic acid dimers) with Mo, Zn, or Sb dithiocarbamates. US-A-4,557,846 relates to lubricating oil friction reducing additives comprising oil soluble hydroxyamide compounds prepared by condensing a dimer carboxylic acid (e.g., linoleic acid dimers) with a hydroxyamine. US-A-4,617,026 relates to fuel friction modifying additives comprising hydroxyl-containing esters of a C₁₂ to C₃₀ monocarboxylic acid and a glycol or trihydric alcohol, wherein the glycol can comprise polyalkylene glycols having 2 to 100 oxyalkylene repeat units. US-A-4,683,069 relates to lubricating oil fuel economy additives comprising glycerol partial esters of C₁₆-C₁₈ fatty acids.

The instability, and hence the need for a stabilization of, compositions containing polycarboxylic acid-glycol esters, ashless dispersant and certain metal lubricating oil additives has been noted in the art. US-A-4,105,571 is directed to storage stable lubricating compositions having improved anti-friction and anti-wear properties containing a zinc dihydrocarbyldithiophosphate, an ester of a polycarboxylic acid and a glycol, and an ashless high molecular weight dispersant, wherein either the zinc or ester component, or both, are predispersed with the ashless dispersant prior to adding them to the lubricating composition. The friction modifying esters are disclosed to include linoleic acid dimers which are esterified with glycol such as diethylene glycol.

US-A-4,388,201 discloses lubricating oil compositions containing such polycarboxylic acid-glycol friction modifier esters in combination with borated or non-borated alkenyl succinimide dispersants, which are stabilized by the addition of small proportions of a co-dispersant comprising an oil-soluble hydrocarbyl substituted mono- or bi-oxazoline or lactone oxazoline.

US-A-4,505,829 discloses lubricating oil compositions containing polycarboxylic acid glycol esters as friction modifiers in combination with hydrocarbon soluble alkenyl succinimide dispersants with reduced tendency towards formation of sediment upon storage. The storage stability is improved by the addition thereto of small proportions of polyol or polyol anhydride partial esters of a fatty acid or an ethoxylated fatty acid, amine or amide compound.

US-A-4,617,134 relates to storage stable lubricating oil compositions comprising an additive combination of a polycarboxylic acid glycol or glycerol ester, as friction modifier, and zinc dihydrocarbyldithiophosphate and an ashless dispersant containing a selected amount of free hydroxyl groups.

US-A-4,684,473 relates to solubilization of oxygenated (hydroxy) esters of a dimer acid (including linoleic dimer esters of polyhydric alcohols) by the incorporation in the lubricating composition of an C₄-C₂₃ oil soluble alkanol or an oil soluble alkyl phosphate. It is disclosed that the selection of the chain length of the alcohol is critical.

The present invention provides an oil soluble mixture useful as an oil additive comprising:

(A) a lubricating oil ashless additive comprising

- (1) ashless dispersants selected from known classes of such additives as defined hereafter; and/or
- (2) polymeric viscosity index improver dispersants selected from known classes of such additives as defined hereafter; and

(B) a demulsifier additive, characterised in that said demulsifier additive (B) comprises the reaction product of

(i) alkylene oxide having from 2 to 10 carbon atoms, and

(ii) an adduct obtained by reacting a polyhydric alcohol with a bis-epoxide containing at least two oxirane rings connected by a C_1 to C_{100} hydrocarbon moiety which optionally contains (a) one or more of alkyl groups, tertiary amino groups and halogens as substituents thereon and/or (b) one or more oxygen atoms, sulfur atoms, carboxy groups, sulfonyl groups, sulfinyl groups, ketone groups, oxirane rings and nitro groups in the carbon chain thereof separated from the carbon atom of the oxirane ring by at least one intervening carbon atom, and wherein said demulsifier contains at least 40 wt.% of oxyalkylene units derived from said alkylene oxides of 3 or more carbon atoms.

The additive mixture may also include a metal detergent component (D) as defined hereafter.

In a preferred embodiment, in particular where the additive mixture is used in concentrates (otherwise referred to as packages), and especially where these contain a metal detergent component (D), the mixture comprises from 0.1 to 5 parts by weight (based on the weight of B) of a compatibility additive (C) comprising an ester or hydroxyamide of a mono- or polycarboxylic acid having a total of from 24 to 90 carbon atoms and at least one carboxylic acid group per molecule, with a mono-, di- or trihydric alcohol.

The invention extends to a lubricating oil additive concentrate containing from 10 to 80 wt.% of an oil soluble mixture according as defined above dissolved in a hydrocarbon oil. The concentrate may preferably comprise:

- from 3 to 45 wt.% of a said ashless dispersant (A)(1)
- from 0.01 to 3 wt.% of a said demulsifier additive (B)
- from 0.0005 to 2 wt.% of a said compatibility additive (C), and
- from 2 to 45 wt.% of a said metal detergent additive (D).

The invention also includes a process for forming a concentrate as described above wherein a said ashless dispersant (A)(1) and a said metal detergent component (D) are pre-mixed at 70 to 130 °C, and wherein a said demulsifier additive (B) and a said compatibility additive (C) are separately mixed, and the separate mixtures are then mixed together.

Thus it has been surprisingly found that improved storage stability is achieved if such a mixture of demulsifier (B) and compatibility additive (C) is first formed and then added to a previously formed mixture of ashless dispersant (A)(1) and metal detergent (D), as compared to mixtures of these components which are prepared using different sorts of mixing.

Finally the invention includes a lubricant composition comprising a concentrate as described above or obtainable by the process described above diluted with 3 to 100 parts by weight (per part by weight of concentrate) of lubricating oil.

DETAILED DESCRIPTION OF THE INVENTION

DISPERSANT COMPONENT A

The dispersant Component A of the oleaginous compositions of this invention can comprise one or more ashless dispersant materials, one or more polymeric viscosity index improver dispersants or mixtures thereof. Ashless dispersants and ashless dispersants admixed with polymeric viscosity index (V.I.) improver dispersants are particularly preferred. When the fully formulated lubricating oil is intended to contain both ashless dispersant and polymeric V.I. improver dispersant, generally they will be introduced to the final oil in separate additive concentrates, since the polymeric V.I. improver dispersants generally are not compatible with concentrates containing ashless dispersants, metal detergents, and many other conventional lubricant additives. Therefore, it will be understood that references herein to amounts and proportions of polymeric VI improver dispersants, unless otherwise indicated, are intended to refer to the final, fully formulated lubricating oil composition, rather than additive concentrates (to be discussed in more detail below).

A-1 Ashless dispersants useful in this invention as Component A comprise nitrogen or ester containing dispersants selected from the group consisting of (i) oil soluble amine salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon-substituted mono and dicarboxylic acids or

their anhydrides or esters; (ii) long chain aliphatic hydrocarbon having a polyamine attached directly thereto; and (iii) Mannich condensation products formed by condensing about a molar proportion of long chain hydrocarbon-substituted phenol with 1 to 2.5 moles of formaldehyde and 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group in (i), (ii) or (iii) is a polymer of a C₂ to C₁₀, e.g., C₂ to C₅, monoolefin, said polymer having a number average molecular weight of at least 900.

A-1(i) The long chain hydrocarbonyl substituted mono or dicarboxylic acid material, i.e. acid, anhydride, or ester, may include long chain hydrocarbon, generally a polyolefin, substituted with an average of at least about 0.8, more generally from 1.0 to 2.0, and preferably from about 1.05 to 1.25, e.g., 1.06 to 1.20, (or 1.10 to 1.20) moles, per mole of polyolefin, of an alpha or beta- unsaturated C₄ to C₁₀ dicarboxylic acid, or anhydride or ester thereof. Exemplary of such dicarboxylic acids, anhydrides and esters thereof are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, etc.

Preferred olefin polymers for reaction with the unsaturated dicarboxylic acids to form Component A-1 ashless dispersants are polymers comprising a major molar amount of C₂ to C₁₀, e.g. C₂ to C₅ monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers can be homopolymers such as polyisobutylene, as well as copolymers of two or more of such olefins such as copolymers of: ethylene and propylene; butylene and isobutylene; propylene and isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₄ to C₁₈ non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene; or a copolymer of ethylene, propylene and 1,4-hexadiene; etc.

In some cases, the olefin polymer may be completely saturated, for example an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

The olefin polymers used in the Component A-1 ashless dispersants will usually have number average molecular weights of at least about 900, more generally within the range of about 1200 and about 5,000, more usually between about 1500 and about 4000. Particularly useful olefin polymers have number average molecular weights within the range of about 1500 and about 3000 with approximately one terminal double bond per polymer chain. An especially useful starting material for highly potent ashless dispersant additives useful in accordance with this invention is polyisobutylene. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatography (GPC) which additionally provides molecular weight distribution information, see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

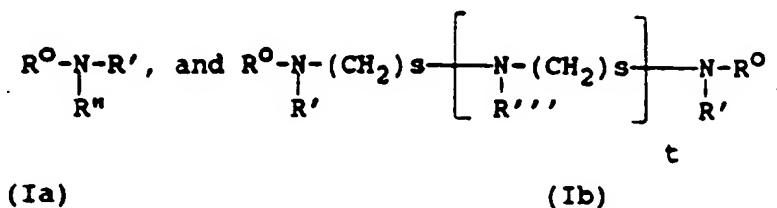
Process for reacting the olefin polymer with the C₄₋₁₀ unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the olefin polymer and the dicarboxylic acid material may be simply heated together as disclosed in US-A-3,361,673 and 3,401,118 to cause a thermal "ene" reaction to take place. Or, the olefin polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polyolefin, at a temperature of 60 to 250 °C, e.g., 120 to 160 °C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer may then be reacted with sufficient unsaturated acid or anhydride at 100 to 250 °C, usually about 180 ° to 235 °C, for about 0.5 to 10, e.g. 3 to 8 hours, so the product obtained will contain the desired number of moles of the unsaturated acid per mole of the halogenated polymer. Processes of this general type are taught in US-A-3,087,436; 3,172,892; 3,272,746 and others.

Alternatively, the olefin polymer, and the unsaturated acid material are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in US-A-3,215,707; 3,231,587; 3,912,764; 4,110,349; 4,234,435; and in GB-A-1,440,219.

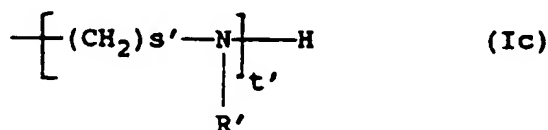
By the use of halogen, about 65 to 95 wt. % of the polyolefin, e.g. polyisobutylene will normally react with the dicarboxylic acid material. Upon carrying out a thermal reaction without the use of halogen or a catalyst, then usually only about 50 to 75 wt. % of the polyisobutylene will react. Chlorination helps increase the reactivity. For convenience, the aforesaid functionality ratios of dicarboxylic acid producing units to polyolefin, e.g., 1.2 to 2.0, are based upon the total amount of polyolefin, that is, the total of both the reacted and unreacted polyolefin, used to make the product.

The dicarboxylic acid producing materials can also be further reacted with amines, alcohols, including polyols, amino-alcohols., to form other useful dispersant additives. Thus, if the acid producing material is to be further reacted, e.g., neutralized, then generally a major proportion of at least 50 percent of the acid units: up to all the acid units will be reacted.

Amine compounds useful as nucleophilic reactants for neutralization of the hydrocarbyl substituted dicarboxylic acid materials include mono- and (preferably) polyamines, most preferably polyalkylene polyamines, of 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and 1 to 12, preferably 2 or 3 to 12, and most preferably 2 or 3 to 9 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 6 hydroxy groups, preferably 1 to 3 hydroxy groups are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:



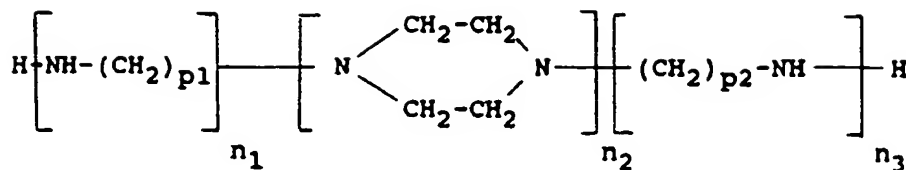
wherein R^0 , R' , R'' and R''' are independently selected from the group consisting of hydrogen; C_1 to C_{25} straight or branched chain alkyl radicals; C_1 to C_{12} alkoxy C_2 to C_6 alkylene radicals; C_2 to C_{12} hydroxy amino alkylene radicals; and C_1 to C_{12} alkylamino C_2 to C_6 alkylene radicals; and wherein R''' can additionally comprise a moiety of the formula:



wherein R' is as defined above, and wherein s and s' can be the same or a different number of from 2 to 6, preferably 2 to 4; and t and t' can be the same or different and are numbers of from 0 to 10, preferably 2 to 7, and most preferably about 3 to 7, with the proviso that the sum of t and t' is not greater than 15. To assure a facile reaction, it is preferred that R^0 , R' , R'' , R''' , s , s' , t and t' be selected in a manner sufficient to provide the compounds of Formulas Ia and Ib with typically at least one primary or secondary amine group, preferably at least two primary or secondary amine groups. This can be achieved by selecting at least one of said R^0 , R' , R'' or R''' groups to be hydrogen or by letting t in Formula Ib be at least one when R''' is H or when the Ic moiety possesses a secondary amino group. The most preferred amine of the above formulas are represented by Formula Ib and contain at least two primary amine groups and at least one, and preferably at least three, secondary amine groups.

Non-limiting examples of suitable amine compounds include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine; triethylene tetramine; tetraethylene pentamine; polypropylene amines such as 1,2-propylene diamine; di-(1,2-propylene)triamine; di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris hydroxymethylaminomethane (THAM); diisopropanol amine; diethanol amine; triethanol amine; mono-, di-, and tri-tallow amines; amino morpholines such as N-(3-aminopropyl)morpholine; and mixtures thereof.

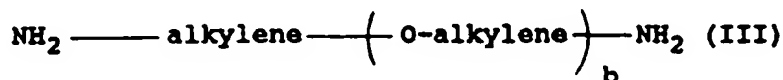
Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula (II):



wherein p_1 and p_2 are the same or different and are each integers of from 1 to 4, and n_1 , n_2 and n_3 are the same or different and are each integers of from 1 to 3. Non-limiting examples of such amines include 2-pentadecyl imidazoline: N-(2-aminoethyl) piperazine.

Commercial mixtures of amine compounds may advantageously be used. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine, tetraethylene pentamine and isomeric piperazines. Low cost poly(ethyleneamines) compounds averaging about 5 to 7 nitrogen atoms per molecule are, available, commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100".

Useful amines also include polyoxyalkylene polyamines such as those of the formulae:



where b has a value of about 3 to 70 and preferably 10 to 35; and



where " c " has a value of about 1 to 40 with the provision that the sum of all the c 's is from about 3 to about 70 and preferably from about 6 to about 35, and R^{iv} is a polyvalent saturated hydrocarbon radical of up to ten carbon atoms wherein the number of substituents on the R^{iv} group is represented by the value of " a ", which is a number of from 3 to 6. The alkylene groups in either formula (III) or (IV) may be straight or branched chains containing about 2 to 7, and preferably about 2 to 4 carbon atoms.

The polyoxyalkylene polyamines of formulas (III) or (IV) above, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have average molecular weights ranging from 200 to 4000 and preferably from 400 to 2000. The preferred polyoxyalkylene polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from 200 to 2000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403", etc.

The amine is readily reacted with the selected dicarboxylic acid material, e.g. alkenyl succinic anhydride, by heating an oil solution containing 5 to 95 wt. % of dicarboxylic acid material to about 100 to 250 °C., preferably 125 to 175 °C., generally for 1 to 10, e.g. 2 to 6 hours until the desired amount of water is removed. The heating is preferably carried out to favor formation of imides or mixtures of imides and amides, rather than amides and amine salts. Reaction ratios of dicarboxylic material to equivalents of amine as well as the other nucleophilic reactants described herein can vary considerably, depending on the reactants and type of bonds formed. Generally from 0.1 to 1.0, preferably from about 0.2 to 0.6, e.g., 0.4 to 0.6, moles of dicarboxylic acid moiety content (e.g., grafted maleic anhydride content) is used per equivalent of nucleophilic reactant, e.g., amine. For example, about 0.8 mole of a pentaamine (having two primary amino groups and five equivalents of nitrogen per molecule) is preferably used to convert into a mixture of amides and imides, the product formed by reacting one mole of olefin with sufficient maleic anhydride to add 1.6 moles of succinic anhydride groups per mole of olefin, i.e., preferably the pentaamine is used in an amount sufficient to provide about 0.4 mole (that is, 1.6 divided by (0.8 x 5) mole) of succinic anhydride moiety per nitrogen equivalent of the amine.

The nitrogen containing ashless dispersants can be further treated by boration as generally taught in US-A-3,087,936 and 3,254,025. This is readily accomplished by treating the selected acyl nitrogen dispersant with a boron compound selected from the class consisting of boron oxide, boron halides, boron acids and esters of boron acids in an amount to provide from about 0.1 atomic proportion of boron for each mole of said acylated nitrogen composition to about 20 atomic proportions of boron for each atomic proportion of nitrogen of said acylated nitrogen composition. Usefully the dispersants of the inventive combination contain from about 0.05 to 2.0 wt. %, e.g. 0.05 to 0.7 wt. % boron based on the total weight of said borated acyl nitrogen compound. The boron, which appears to be in the product as dehydrated boric acid polymers (primarily $(\text{HBO}_2)_3$), is believed to attach to the dispersant imides and diimides as amine salts, e.g., the metaborate salt of said diimide.

Treating is readily carried out by adding from about 0.05 to 4, e.g., 1 to 3 wt. % (based on the weight of said acyl nitrogen compound) of said boron compound, preferably boric acid which is most usually added as a slurry to said acyl nitrogen compound and heating with stirring at from about 135°C. to 190, e.g., 140-170°C., for from 1 to 5 hours followed by nitrogen stripping at said temperature ranges. Or, the boron treatment can be carried out by adding boric acid to the hot reaction mixture of the dicarboxylic acid material and amine while removing water.

The tris(hydroxymethyl) amino methane (THAM) can be reacted with the aforesaid acid material to form amides, imides or ester type additives as taught by GB-A-984,409, or to form oxazoline compounds and borated oxazoline compounds as described, for example, in US-A-4,102,798; 4,116,876 and 4,113,639.

The ashless dispersants may also be esters derived from the aforesaid long chain hydrocarbon substituted dicarboxylic acid material and from hydroxy compounds such as monohydric and polyhydric alcohols or aromatic compounds such as phenols and naphthols. The polyhydric alcohols are the most preferred hydroxy compound and preferably contain from 2 to about 10 hydroxy radicals, for example, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and other alkylene glycols in which the alkylene radical contains from 2 to about 8 carbon atoms. Other useful polyhydric alcohols include glycerol, mono-oleate of glycerol, monostearate of glycerol, monomethyl ether of glycerol, pentaerythritol, dipentaerythritol, and mixtures thereof.

The ester dispersant may also be derived from unsaturated alcohols such as allyl alcohol, cinnamyl alcohol, propargyl alcohol, 1-cyclohexane-3-ol, and oleyl alcohol. Still other classes of the alcohols capable of yielding the esters of this invention comprise the ether-alcohols and amino-alcohols including, for example, the oxy-alkylene-, oxy-arylene-, amino-alkylene-, and amino-arylene-substituted alcohols having one or more oxy-alkylene, amino-alkylene, amino-arylene or oxy-arylene radicals. They are exemplified by Cellosolve (commercial denomination), Carbitol, N,N,N',N'-tetrahydroxy-trimethylene diamine, and ether-alcohols having up to about 150 oxy-alkylene radicals in which the alkylene radical contains from 1 to about 8 carbon atoms.

The ester dispersant may be di-esters of succinic acids or acidic esters, i.e., partially esterified succinic acids; as well as partially esterified polyhydric alcohols or phenols, i.e., esters having free alcohols or phenolic hydroxyl radicals. Mixtures of the above illustrated esters likewise are contemplated within the scope of this invention.

The ester dispersant may be prepared by one of several known methods as illustrated for example in US-A-3,381,022. The ester dispersants may also be borated, similar to the nitrogen containing dispersants, as described above.

Hydroxyamines which can be reacted with the aforesaid long chain hydrocarbon substituted dicarboxylic acid materials to form dispersants include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1, 3-propanediol, 2-amino-2-ethyl-1, 3-propanediol, N-(beta-hydroxy-propyl)-N'-(beta-amino-ethyl)-piperazine, tris-(hydroxymethyl) amino-methane (also known as trimethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)ethylamine, and the like. Mixtures of these or similar amines can also be employed. The above description of nucleophilic reactants suitable for reaction with the hydrocarbyl substituted dicarboxylic acid or anhydride includes amines, alcohols, and compounds of mixed amine and hydroxy containing reactive functional groups, i.e., amino-alcohols.

A preferred group of ashless dispersants are those derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene and polyoxypropylene amines, e.g., polyoxypropylene diamine, trimethylolaminomethane and pentaerythritol, and combinations thereof. One particularly preferred ashless dispersant combination involves a combination of (i) polyisobutene substituted with succinic anhydride groups and reacted with (ii) a hydroxy compound, e.g., pentaerythritol, (iii) a polyoxyalkylene

polyamine, e.g., polyoxypropylene diamine, and (iv) a polyalkylene polyamine, e.g., polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles each of (ii) and (iv) and about 0.3 to about 2 moles of (iii) per mole of (i) as described in US-A-3,804,763. Another preferred ashless dispersant combination involves the combination of (i) polyisobutenyl succinic anhydride with (ii) a polyalkylene polyamine, e.g., tetraethylene pentamine, and (iii) a polyhydric alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trimethylolaminomethane as described in US-A-3,632,511.

A-1(ii) Also useful as ashless nitrogen-containing dispersant in this invention are dispersants wherein a nitrogen containing polyamine is attached directly to the long chain aliphatic hydrocarbon as shown in US-A-3,275,554 and 3,565,804 where the halogen group on the halogenated hydrocarbon is displaced with various alkylene polyamines.

A-1(iii) Another class of nitrogen containing dispersants which may be used are those containing Mannich base or Mannich condensation products as they are known in the art. Such Mannich condensation products generally are prepared by condensing about 1 mole of a high molecular weight hydrocarbyl substituted mono- or polyhydroxy benzene (e.g., having a number average molecular weight of 1,000 or greater) with about 1 to 2.5 moles of formaldehyde or paraformaldehyde and about 0.5 to 2 moles polyalkylene polyamine as disclosed, e.g., in US-A-3,442,808; 3,649,229 and 3,798,165. Such Mannich condensation products may include a long chain, high molecular weight hydrocarbon on the phenol group or may be reacted with a compound containing such a hydrocarbon, e.g., polyalkenyl succinic anhydride as shown in said aforementioned US-A-3,442,808.

A-2 Examples of suitable polymeric viscosity index improvers dispersants include:

(i) polymers comprised of C_4 to C_{24} unsaturated esters of vinyl alcohol or C_3 to C_{10} unsaturated mono- or dicarboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons;

(ii) polymers of C_2 to C_{20} olefin with unsaturated C_3 to C_{10} mono- or dicarboxylic acid neutralized with amine, hydroxy amine or alcohols; and

(iii) polymers of ethylene with a C_3 to C_{20} olefin further reacted either by grafting C_4 to C_{20} unsaturated nitrogen containing monomers thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol.

In these polymers the amine, hydroxy amine or alcohol "mono- or poly-hydric" may be as described above in relation to the ashless dispersant compounds.

It is preferred that the polymeric viscosity index improver dispersant have a number average molecular weight range as by vapor phase osmometry, membrane osmometry, or gel permeation chromatography, of 1000 to 2,000,000; preferably 5,000 to 250,000 and most preferably 10,000 to 200,000. It is also preferred that the polymers of group (i) comprise a major weight amount of unsaturated ester and a minor, e.g., 0.1 to 40, preferably 1 to 20 wt.% of a nitrogen containing unsaturated monomer, said wt.% based on total polymer. Preferably the polymer group (ii) comprises 0.1 to 10 moles of olefin, preferably 0.2 to 5 moles C_2 - C_{20} aliphatic or aromatic olefin moieties per mole of unsaturated carboxylic acid moiety and that from 50% to 100% of the acid moieties are neutralized. Preferably the polymer of group (iii) comprises an ethylene copolymer of 25 to 80 wt.% ethylene with 75 to 20 wt.% C_3 to C_{20} mono- and/or diolefin, 100 parts by weight of ethylene copolymer being grafted with either 0.1 to 40, preferably 1 to 20 parts by weight unsaturated nitrogen containing monomer, or being grafted with 0.01 to 5 parts by weight of unsaturated C_3 to C_{10} mono- or dicarboxylic acid, which acid is 50% or more neutralized.

The unsaturated carboxylic acids used in (i), (ii) and (iii) above will preferably contain 3 to 10, more usually 3 or 4 carbon atoms, and may be mono carboxylic such as methacrylic and acrylic acids or dicarboxylic such as maleic acid, maleic anhydride, fumaric acid.

Examples of unsaturated esters that may be used include aliphatic saturated mono alcohols of at least 1 carbon atom, and preferably of from 12 to 20 carbon atoms such as decyl acrylate, lauryl acrylate, stearyl acrylate, eicosanyl acrylate, docosanyl acrylate, decyl methacrylate, diamyl fumarate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

Other esters include the vinyl alcohol esters of C_2 to C_{22} fatty or mono carboxylic acids, preferably saturated such as vinyl acetate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof.

Such ester polymers may be grafted with, or the ester copolymerized with, polymerizable unsaturated nitrogen-containing monomers to impart dispersancy to the V.I. improvers. Examples of suitable unsaturated nitrogen-containing monomers include those containing 4 to 20 carbon atoms such as amino substituted olefins as p-(beta-diethylaminoethyl)styrene; basic nitrogen-containing heterocycles carrying

a polymerizable ethylenically unsaturated substituent, e.g., the vinyl pyridines and the vinyl alkyl pyridines such as 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinyl pyridine, 2-vinyl-pyridine, 4-vinyl-pyridine, 3-vinyl-pyridine, 3-methyl-5-vinyl-pyridine, 4-methyl-2-vinyl-pyridine, 4-ethyl-2-vinyl-pyridine and 2-butyl-5-vinyl-pyridine and the like.

5 N-vinyl lactams are also suitable, e.g., N-vinyl pyrrolidones or N-vinyl piperidones. The vinyl radical preferably is unsubstituted ($\text{CH}_2 = \text{CH}-$), but it may be mono substituted with an aliphatic hydrocarbon group of 1 to 2 carbon atoms, such a methyl or ethyl.

The vinyl pyrrolidones are preferred and are exemplified by N-vinyl pyrrolidone, N-(1-methylvinyl) pyrrolidone, N-vinyl-5-methyl pyrrolidone, N-vinyl-3,3-dimethylpyrrolidone, N-vinyl-5-ethyl pyrrolidone, N-vinyl-4-butyl pyrrolidone N-ethyl-3-vinyl pyrrolidone, N-butyl-5-vinyl pyrrolidone, 3-vinyl pyrrolidone, 4-vinyl pyrrolidone, 5-vinyl pyrrolidone and 5-cyclohexyl-N-vinyl pyrrolidone, and the like.

Examples of olefins which could be used to prepare the copolymers of (ii) and (iii) above include mono-olefins such as "propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-decene, 1-dodecene, styrene, etc.

15 Representative non-limiting examples of diolefins that can be used in (iii) include 1,4-hexadiene, 1,5-heptadiene, 1,6-octadiene, 5-methyl-1-4-hexadiene, 1,4-cyclohexadiene, 1,5-cyclo-octadiene, vinyl-cyclohexane, dicyclopentenyl and 4,4'-dicyclohexenyl such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo(2,2,1)-hepta-2,5-diene, alkenyl, alkylidene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene.

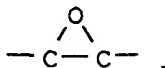
20 Typical polymeric viscosity index improver-dispersants include copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, alkyl fumarate-vinyl acetate N-vinyl pyrrolidone copolymers, post-grafted interpolymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, e.g., see US-A-4,089,794; 4,160,739; 4,137,185; or copolymers of ethylene and propylene reacted or grafted with nitrogen compounds such as shown in US-A-4,068,056; 4,068,058; 4,146,489; 4,149,984; styrene/maleic anhydride polymers post-reacted with alcohols and amines, ethoxylated derivatives of acrylate polymers, for example, see US-A-3,702,300. Also useful are styrene-isobutylene, and styrene-maleic anhydride copolymers and terpolymers and the like substituted with nitrogen-containing compounds (e.g., polyalkylene polyamines, piperidines, morpholines, hydrazines, and the like) and Mannich base condensation product derivatives, as disclosed in US-A-3,493,520; 3,558,743; 3,634,493; 3,684,713; 3,933,761; 3,956 149; 3,959,159; 4,029,702; and 4,424,317; HU-B-25,896; SU-A-235,232, and 1,121,268; and GB-A-2,124,633.

DEMULSIFIER COMPONENT B

35 The lubricating oil demulsifier additives of this invention are the water insoluble, at least partially oil soluble product of the reaction of (i) an alkylene oxide having from 2 to 10 carbon atoms and (ii) an adduct obtained by reacting a bis-epoxide, preferably a diglycidyl ether of bis-phenol A, and a polyhydric alcohol, preferably a polyoxyalkylene glycol.

40 In making the demulsifiers of this invention, a first adduct is made by reacting a bis-epoxide with a polyhydric alcohol.

The bis-epoxides are compounds containing at least two oxirane rings, i.e.,



45 These oxirane rings are connected or joined by hydrocarbon moieties or by hydrocarbon moieties containing at least one hetero atom or group (as defined hereinafter). The hydrocarbon moieties contain from 1 to 100 carbon atoms. They include the alkylene, cycloalkylene, alkenylene, arylene, aralkenylene and alkarylene radicals. Typical alkylene radicals are those containing from 1 to 100 carbon atoms, more typically from 1 to 50 carbon atoms. The alkylene radicals may be straight chain or branched and may contain from 1 to 100 carbon atoms, preferably from 1 to 50 carbon atoms. Typical cycloalkylene radicals are those containing from 4 to 16 ring carbon atoms. The cycloalkylene radicals may contain alkyl substituents, e.g., $\text{C}_1\text{-C}_8$ alkyl, on one or more ring carbon atoms. Typical arylene radicals are those containing from 6 to 12 ring carbons, e.g., phenylene, naphthylene and biphenylene. Typical alkarylene and aralkylene radicals are those containing from 7 to 100 carbon atoms, preferably from 7 to 50 carbon atoms. The hydrocarbon moieties joining the oxirane rings may contain substituent groups thereon. The substituent

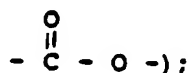
groups are those which are substantially inert or unreactive at ambient conditions with the oxirane ring. As used in the specification the term "substantially inert and unreactive at ambient conditions" is intended to mean that the atom or group is substantially inert to chemical reactions at ambient temperatures and pressure with the oxirane ring so as not to materially interfere in an adverse manner with the preparation and/or functioning of the compositions, additives, compounds, of this invention in the context of its intended use. For example, small amounts of these atoms or groups can undergo minimal reaction with the oxirane ring without preventing the making and using of the invention as described herein. In other words, such reaction, while technically discernable, would not be sufficient to deter the practical worker of ordinary skill in the art from making and using the invention for its intended purposes. Suitable substituent groups are alkyl groups, hydroxyl groups, tertiary amino groups and halogens. When more than one substituent is present they may be the same or different.

It is to be understood that while many substituent groups are substantially inert or unreactive at ambient conditions with the oxirane ring, they will react with the oxirane ring under conditions effective to allow reaction of the oxirane ring with the reactive hydroxy groups of the polyhydric alcohols. Whether these groups are suitable substituent groups which can be present on the bis-epoxide depends, in part, upon their reactivity with the oxirane ring. Generally, if they are substantially more reactive with the oxirane ring than the oxirane ring is with the reactive hydroxy group, they will tend to materially interfere in an adverse manner with the preparation of the intended demulsifiers of this invention and are, therefore, unsuitable. If, however, their reactivity with the oxirane ring is less than or generally similar to the reactivity of the oxirane ring with the reactive hydroxy groups, they will not materially interfere in an adverse manner with the preparation of the demulsifiers of the present invention and may be present on the bis-epoxide, particularly if the epoxide groups are present in excess relative to the substituent groups. An example of such a reactive but suitable group is the hydroxyl group. An example of an unsuitable substituent group is a primary amino group.

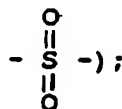
The hydrocarbon moieties containing at least one hetero atom or group are the hydrocarbon moieties described above which contain at least one hetero atom or group in the chain. The hetero atoms or groups are those that are substantially unreactive at ambient conditions with the oxirane rings. When more than one hetero atom or group is present they may be the same or different. The hetero atoms or groups are separated from the carbon atom of the oxirane ring by at least one intervening carbon atom. These hetero atom or group containing hydrocarbon moieties may contain at least one substituent group on at least one carbon atom. These substituent groups are the same as those described above as being suitable for the hydrocarbon moieties.

Suitable hetero atoms or groups which may be in the carbon chain of the hydrocarbon moiety are:

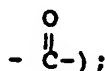
oxygen atoms (i.e., -O- or ether linkages in the carbon chain);
sulfur atoms (i.e., -S- or thioether linkages in the carbon chain);
carboxy groups (i.e.,



sulfonyl group (i.e.,



ketone group (i.e.,



sulfinyl group (i.e.,



an oxirane ring (i.e.,



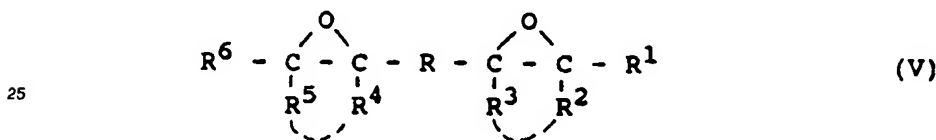
and

15 nitro group.

As mentioned hereinafore the bis-epoxides of the present invention contain at least two oxirane rings or epoxide moieties. It is critical that the bis-epoxide contain at least two oxirane rings in the same molecule.

The bis-epoxides useful in the instant invention are well known in the art and are generally commercially available or may readily be prepared by conventional and well known methods.

20 The bis-epoxides include those represented by the general formula



wherein:

30 R is a divalent hydrocarbon radical, a substituted divalent hydrocarbon radical, a divalent hydrocarbon radical containing at least one hetero atom or group, and a substituted divalent hydrocarbon radical containing at least one hetero atom or group;

R¹ and R⁶ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, and oxirane containing radicals;

R² and R³ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, monovalent oxirane containing radicals, divalent hydrocarbon radicals, and substituted divalent hydrocarbon radicals, with the proviso that if R² or R³ is a divalent hydrocarbon radical or substituted divalent hydrocarbon radical then both R² and R³ must be divalent hydrocarbon radicals or substituted divalent hydrocarbon radicals that together with the two carbon atoms of the oxirane ring form a cyclic structure; and

R⁴ and R⁵ are independently selected from hydrogen, monovalent hydrocarbon radicals, substituted monovalent hydrocarbon radicals, monovalent hydrocarbon radicals containing at least one hetero atom or group, substituted monovalent hydrocarbon radicals containing at least one hetero atom or group, monovalent oxirane containing radicals, divalent hydrocarbon radicals, and substituted divalent hydrocarbon radicals, with the proviso that if R⁴ or R⁵ is a divalent hydrocarbon radical or substituted divalent hydrocarbon radical then both R⁴ and R⁵ must be divalent hydrocarbon radicals or substituted divalent hydrocarbon radicals that together with the two carbon atoms of the oxirane ring form a cyclic structure.

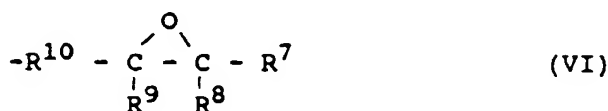
The monovalent hydrocarbon radicals represented by R¹ - R⁶ generally contain from 1 to 100 carbon atoms. These hydrocarbon radicals include alkyl, alkenyl, cycloalkyl, aryl, aralkyl, and alkaryl radicals. The alkyl radicals may contain from 1 to 100, preferably from 1 to 50, carbon atoms and may be straight chain or branched. The alkenyl radicals may contain from 2 to 100 carbons, preferably from 2 to 50 carbon atoms, and may be straight chain or branched. Preferred cycloalkyl radicals are those containing from 4 to 12 ring carbon atoms, e.g., cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl. These cycloalkyl radicals may contain substituent groups, preferably alkyl groups, on the ring carbon atoms, e.g., methylcyclohexyl, 1,3-dimethylcyclopentyl. The preferred alkenyl radicals are those containing from 2 to 30 carbon atoms, e.g.,

ethenyl, 1-propenyl, 2-propenyl. The preferred aryl radicals are those containing from 6 to 12 ring carbon atoms, i.e., phenyl, naphthyl, and biphenyl. The preferred aralkyl and alkaryl radicals are those containing from 7 to 30 carbon atoms, e.g., p-tolyl, 2,6-xylyl, 2,4,6-trimethylphenyl, 2-isopropylphenyl, benzyl, 2-phenylethyl, 4-phenylbutyl. The substituted monovalent hydrocarbon radicals represented by R¹ - R⁶ are the monovalent hydrocarbon radicals described hereinafore which contain at least one substituent group thereon. The substituent groups are such that they are substantially unreactive under ambient conditions with the oxirane moieties. When more than one substituent group is present they may be the same or different.

The monovalent hydrocarbon radicals containing at least one hetero atom or group are the monovalent hydrocarbon radicals described hereinafore which contain at least one hetero atom or group in the carbon chain. The hetero atom or group is separated from the carbon of the oxirane ring by at least one intervening carbon atom. When more than one hetero atom or group is present they may be the same or different. The hetero atoms or groups are those that are substantially unreactive under ambient conditions with the oxirane ring. These hetero atoms or groups are those described hereinafore.

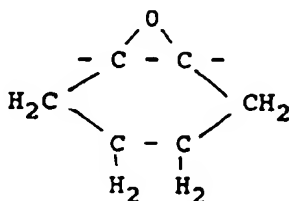
The substituted monovalent hydrocarbon radicals containing at least one hetero atom or group are the substituted monovalent hydrocarbon radicals containing at least one hetero atom or group described above which contain at least one substituent group on at least one carbon atom. The substituent groups are those described hereinafore.

The oxirane radicals represented by R¹ - R⁶ may be represented by the formula

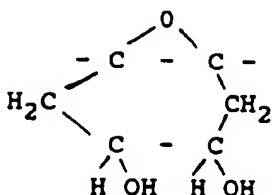


wherein:

R⁷ has the same meaning as R¹, R⁸ - R⁹ have the same meaning as R² - R³, and R¹⁰ has the same meaning as R in Formula V. The divalent hydrocarbon radicals represented by R² - R⁵ and R⁸ - R⁹ generally are aliphatic acyclic radicals and contain from 1 to 5 carbon atoms. Preferred divalent hydrocarbon radicals are the alkylene radicals. Preferred alkylene radicals are those that, together with the two carbon atoms of the oxirane ring, form a cyclic structure containing from 4 to 8 ring carbon atoms. Thus, for example, if R³ and R⁴ are both ethylene radicals the resultant cyclic structure formed with the two carbon atoms of the oxirane ring is a cyclohexylene oxide, i.e.,



The divalent substituted hydrocarbon radicals represented by R² - R⁵ and R⁸ - R⁹ are the divalent hydrocarbon radicals described above which contain at least one substituent group on at least one carbon atom. Thus, for example, if R³ and R⁴ are both hydroxy substituted ethylene radicals, the resultant cyclic structure formed with the two carbon atoms of the oxirane ring may be represented by the formula:



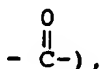
The divalent hydrocarbon radicals represented by R and R¹⁰ generally contain from 1 to 100 carbon atoms, preferably from 1 to 50 carbon atoms. They may be aliphatic, aromatic or aliphatic-aromatic. If they are aliphatic they may be saturated or unsaturated, acyclic or alicyclic. They include alkylene, cycloalkylene, alkenylene, arylene, aralkylene, and alkarylene radicals. The alkylene radicals may be straight chain or branched. Preferred alkylene radicals are those containing from 1 to 50 carbon atoms. Preferred alkenylene radicals are those containing from 2 to 50 carbon atoms. Preferred cycloalkylene radicals are those containing from 4 to 12 ring carbon atoms. The cycloalkylene radicals may contain substituents, preferably alkyls, on the ring carbon atoms.

It is to be understood that the term "arylene" as used in the specification and the appended claims is not intended to limit the divalent aromatic moiety represented by R and R¹⁰ to benzene. Accordingly, it is to be understood that the divalent aromatic moiety can be a single aromatic nucleus such as a benzene nucleus, a pyridine nucleus, a thiophene nucleus, a 1,2,3,4-tetra-hydronaphthalene nucleus, etc., or a polynuclear aromatic moiety. Such polynuclear moieties can be of the fused type; that is, wherein at least one aromatic nucleus is fused at two points to another nucleus such as found in naphthalene, anthracene, the azanaphthalenes. Alternatively, such polynuclear aromatic moieties can be of the linked type wherein at least two nuclei (either mono- or polynuclear) are linked through bridging linkages to each other. Such bridging linkages can be chosen from the group consisting of carbon-to-carbon single bonds, ether linkages, keto linkages, sulfide linkages, polysulfide linkages of 2 to 6 sulfur atoms, sulfinyl linkages, sulfonyl linkages, methylene linkages, alkylene linkages, di-(lower alkyl)-methylene linkages, lower alkylene ether linkages, alkylene keto linkages, lower alkylene sulfur linkages, lower alkylene polysulfide linkages of 2 to 6 carbon atoms, amino linkages, polyamino linkages and mixtures of such divalent bridging linkages.

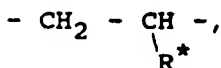
When the divalent aromatic moiety, Ar, is a linked polynuclear aromatic moiety it can be represented by the general formula



wherein r is an integer of 1 to 10, preferably 1 to 8, more preferably 1, 2 or 3; Ar is a divalent aromatic moiety as described above, and each Lng is a bridging linkage individually chosen from the group consisting of carbon-to-carbon single bonds, ether linkages (e.g. -O-), keto linkages (e.g.,

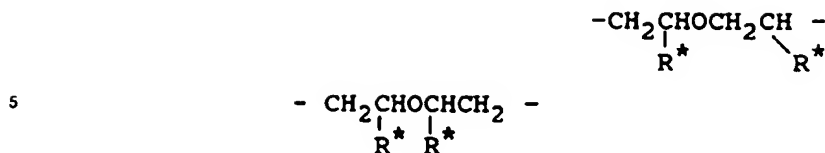


sulfide linkages (e.g., -S-), polysulfide linkages of 2 to 6 sulfur atoms (e.g., -S₂-), sulfinyl linkages (e.g., -S(O)-), sulfonyl linkages (e.g., -S(O)₂-), lower alkylene linkages (e.g., -CH₂-, -CH₂-CH₂-),



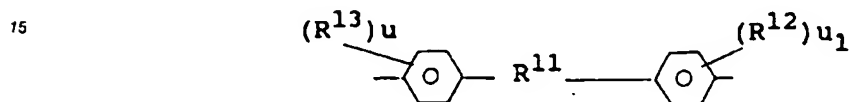
etc.),

di (lower alkyl) -methylene linkages (e.g., -CR²₂-), lower alkylene ether linkages (e.g., -CH₂-O-, -CH₂-O-CH₂-, -CH₂-CH₂-O-, -CH₂CH₂OCH₂CH₂-),



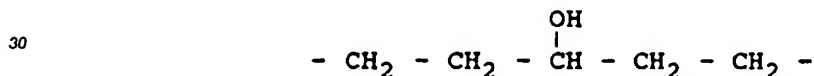
.) lower alkylene sulfide linkages (e.g., wherein one or more -O-'s in the lower alkylene ether linkages is replaced with an -S- atom), lower alkylene polysulfide linkages (e.g., wherein one or more -O-'s is replaced with a -S₂ to -S₆ group), with R* being a lower alkyl group.

Illustrative of such linked polynuclear aromatic moieties are those represented by the formula



20 wherein R¹² and R¹³ are independently selected from hydrogen and alkyl radicals, preferably alkyl radicals containing from 1 to 20 carbon atoms; R¹¹ is selected from alkylene, alkylidene, cycloalkylene, and cycloalkylidene radicals; and u and u¹ are independently selected from integers having a value of from 1 to 4.

25 The divalent substituted hydrocarbon radicals represented by R and R¹⁰ are those divalent hydrocarbon radicals described above which contain at least one substituent group of the type described hereinafore. Thus, for example, if the divalent hydrocarbon radical is a C₅ alkylene, the corresponding divalent substitute hydrocarbon radical, e.g., hydroxyl substituted radical, may be



When more than one substituent group is present they may be the same or different.

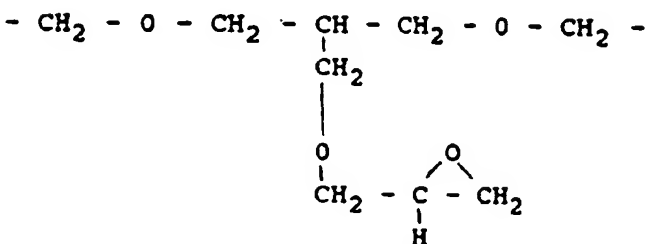
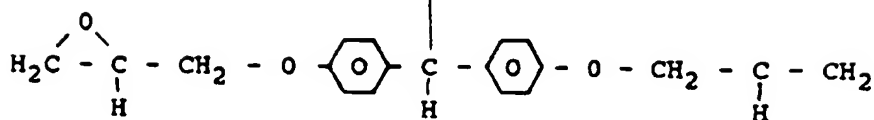
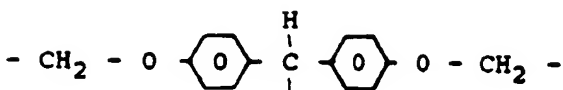
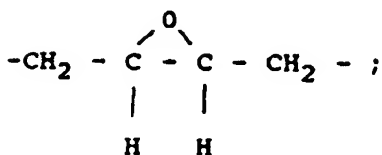
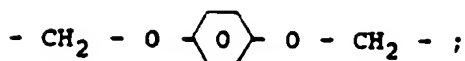
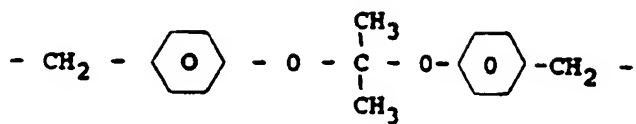
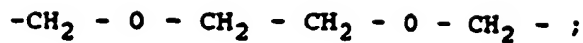
35 The divalent hydrocarbon radicals containing at least one hetero atom or group are those divalent hydrocarbon radicals described hereinafore which contain at least one hetero atom or group. These hetero atoms or groups are those described hereinafore. Some illustrative non-limiting examples of divalent hydrocarbon radicals containing at least one hetero atom or group include:

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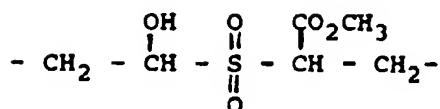
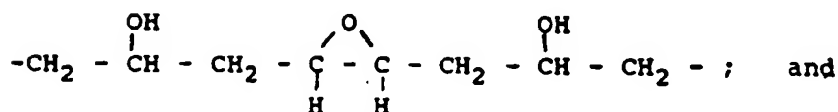
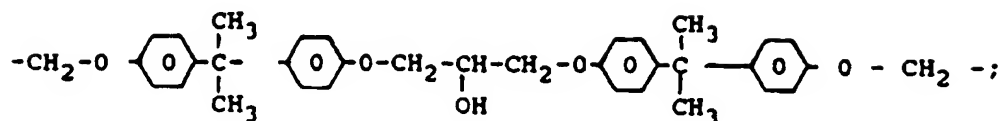
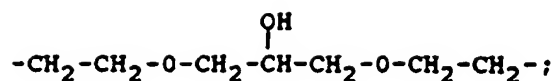
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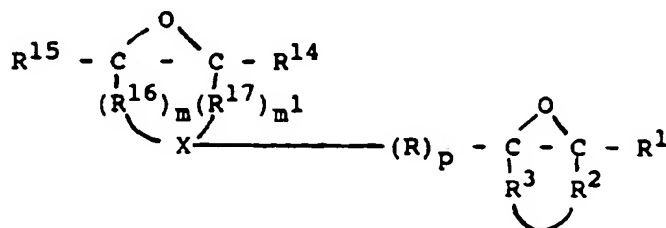
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The divalent substituted hydrocarbon radicals containing at least one hetero atom or group are those divalent hydrocarbon radicals containing at least one hetero atom or group described above which contain at least one substituent group of the type described hereinabove. Some illustrative non-limiting examples of divalent substituted hydrocarbon radicals containing at least one hetero atom or group include:



Also included within the scope of the bis-epoxides of the instant invention are these represented by the formula (VII)

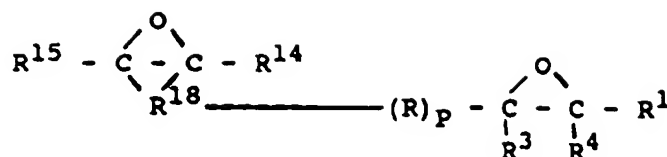


wherein:

40 R and R¹⁻³ are as defined hereinafore; R¹⁴ and R¹⁵ independently have the same meaning as R¹; X is an aromatic moiety; R¹⁶ and R¹⁷ are independently selected from divalent aliphatic acyclic hydrocarbon radicals and divalent substituted aliphatic acyclic hydrocarbon radicals which together with the two carbon atoms of the oxirane ring and the two adjacent ring carbon atoms of the aromatic moiety X form a cyclic structure; m and m' are independently zero or one with the proviso that the sum of m plus m' is at least
45 one; and p is zero or one.

The aromatic moieties represented by X are preferably those containing from 6 to 12 ring carbon atoms, e.g., benzene, naphthalene, and biphenyl. The aromatic moieties may contain one or more substituents on one or more ring carbon atoms. These substituents are those which are substantially unreactive at ambient conditions, e.g., temperature and pressure, with the oxirane ring. They include, for example, alkyl, hydroxyl, nitro, and the like.

Also falling within the scope of the bis-epoxides of the instant invention are those represented by the formula (VIII):



wherein:

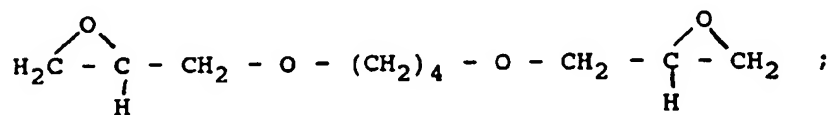
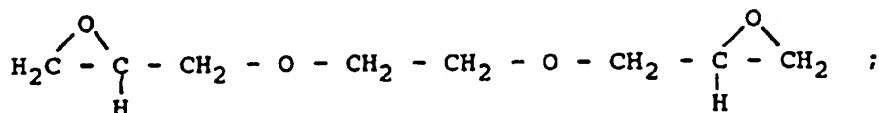
10 R, R¹-R³, R¹⁴-R¹⁵ and p are as defined hereinafore; and R¹⁸ is independently selected from divalent hydrocarbon radicals or a substituted divalent hydrocarbon radicals which together with the two carbon atoms of the oxirane ring forms a cyclic preferably cycloaliphatic, structure.

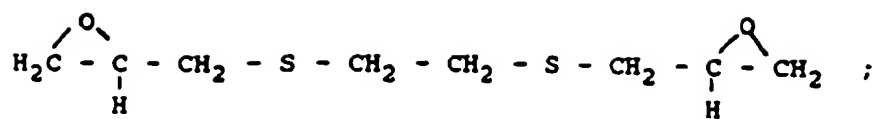
The divalent hydrocarbon or substituted divalent hydrocarbon radicals represented by R¹⁸ preferably contain from 2 to 14 carbon atoms so as to form, together with the two carbon atoms of the oxirane ring, a 4 to 16 membered ring structure, preferably a cycloaliphatic ring. The preferred divalent hydrocarbon radicals are the divalent aliphatic hydrocarbon radicals, preferably the alkylene radicals.

The divalent aliphatic hydrocarbon radicals represented by R¹⁸ may contain one or more substituent groups on one or more ring carbon atoms. The substituents are selected from those that are substantially unreactive under ambient conditions with the oxirane ring, e.g., alkyl, hydroxyl, and the like.

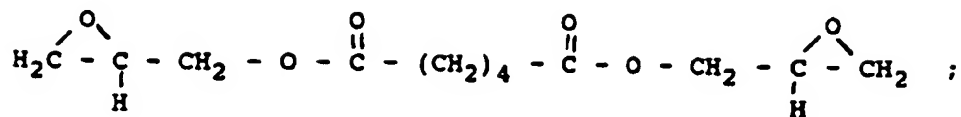
20 Preferred bis-epoxides of the instant invention are those wherein the oxirane rings (preferably at least one of which is a terminal or end oxirane ring) are unhindered. By unhindered is meant that the oxirane ring contains one secondary carbon atom, i.e., having two hydrogens bonded thereto, and preferably contains one secondary carbon atom and one tertiary carbon atom, i.e., having one hydrogen bonded thereto. Thus, for example, an unhindered bis-epoxide of Formula V is one wherein R¹, R², R⁵, and R⁶ are hydrogen, preferably one wherein R¹-R³ and R⁴-R⁶ are all hydrogen.

Some illustrative non-limiting Examples of the bis-epoxides of the instant invention include:

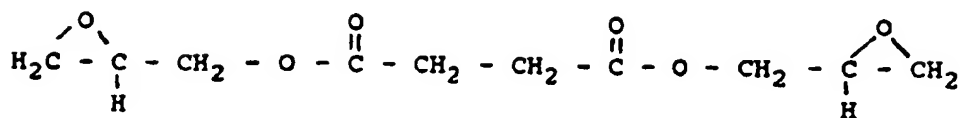




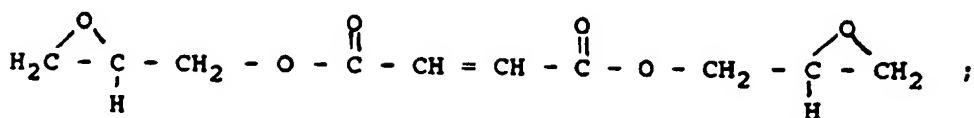
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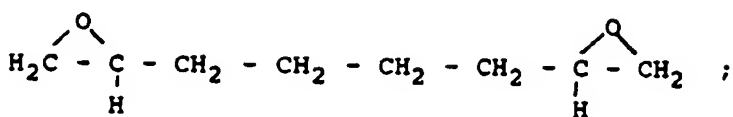
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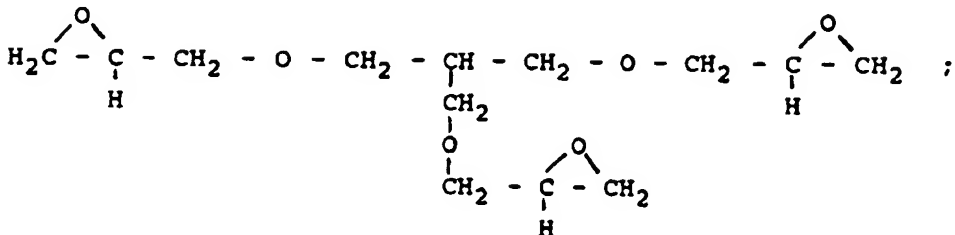
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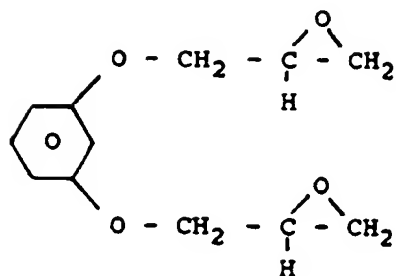


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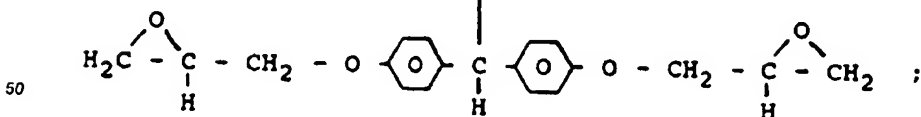
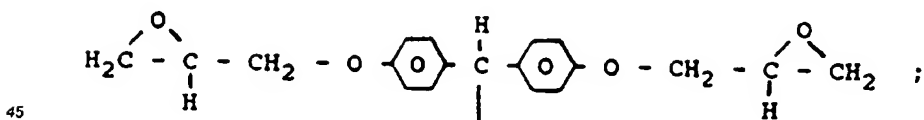
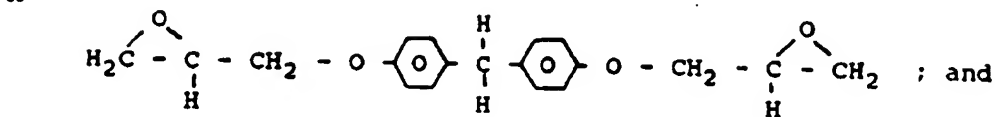
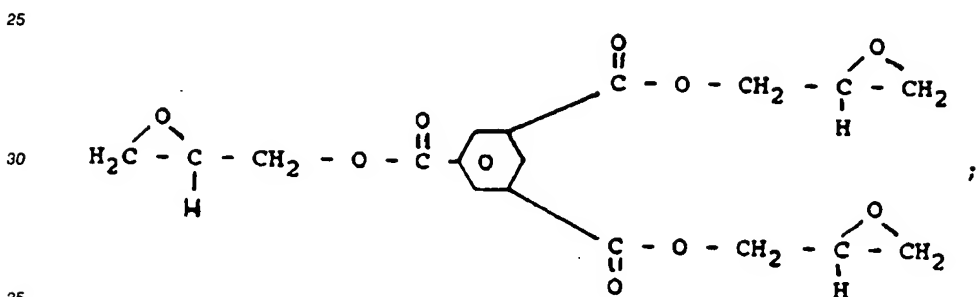
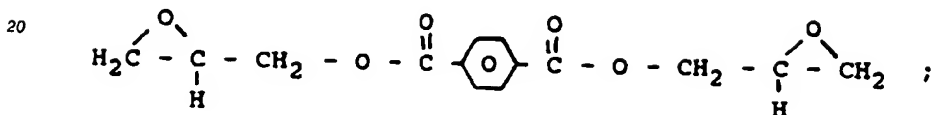
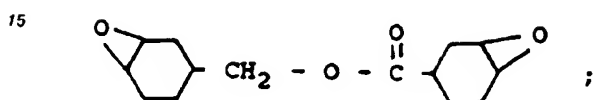
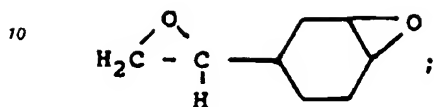


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New York, 1967; and in US-A-Nos. 3,477,990 and 3,408,422.

The epoxy resins include those compounds possessing one or two terminal epoxy groups. These bis-epoxides are saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and are substituted, if desired, with non-interfering substituents, such as halogen atoms, hydroxyl groups, ether radicals, and the like.

Preferred bis-epoxides are the glycidyl polyethers of polyhydric phenols and polyhydric alcohols, especially the glycidyl polyethers of 2,2-bis(4-hydroxyphenyl) propane having an average molecular weight between 300 and 3,000 and an epoxide equivalent weight (WPE) between 140 and 2,000. Especially preferred are the diglycidyl polyethers of 2,2-bis(4-hydroxyphenyl) propane having a WPE between 140 and 500 and an average molecular weight of from 300 to 900.

Other suitable epoxy compounds include those compounds derived from polyhydric phenols and having at least one vicinal epoxy group wherein the carbon-to-carbon bonds within the six-membered ring are saturated. Such epoxy resins may be obtained by at least two well-known techniques, i.e., by the hydrogenation of glycidyl polyethers of polyhydric phenols or (2) by the reaction of hydrogenated polyhydric phenols with epichlorohydrin in the presence of a suitable catalyst such as Lewis acids, i.e., boron trihalides and complexes thereof, and subsequent dehydrochlorination in an alkaline medium. The method of preparation forms no part of the present invention and the resulting saturated epoxy resins derived by either method are suitable in the present compositions.

Briefly, the first method comprises the hydrogenation of glycidyl polyethers of polyhydric phenols with hydrogen in the presence of a catalyst consisting of rhodium and/or ruthenium supported on an inert carrier at a temperature below about 50°C. This method is thoroughly disclosed and described in US-A-3,336,241, issued Aug. 15, 1967.

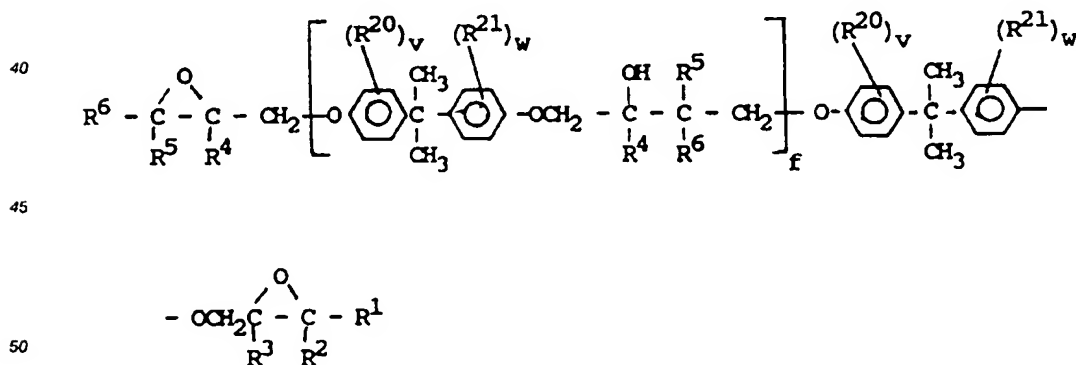
The hydrogenated epoxy compounds prepared by the process disclosed in US-A-3,336,241 are suitable for use in the present compositions.

The second method comprises the condensation of a hydrogenated polyphenol with an epichlorohydrin, such as epichlorohydrin, in the presence of a suitable catalyst such as BF₃, followed by dehydrohalogenation in the presence of caustic. When the phenol is hydrogenated Bisphenol A, the resulting saturated epoxy compound is sometimes referred to as "diepoxidized hydrogenated Bisphenol A," or more properly as the diglycidyl ether of 2,2-bis(4-cyclohexanol) propane.

In any event, the term "saturated epoxy resin," as used herein shall be deemed to mean the glycidyl ethers of polyhydric phenols wherein the aromatic ring structure of the phenols have been or are saturated.

Preferred saturated epoxy resins are the hydrogenated resins prepared by the process described in US-A-3,336,241. More preferred are the hydrogenated glycidyl ethers of 2,2-bis(4-hydroxyphenyl) propane, sometimes called the diglycidyl ethers of 2,2-bis(4-cyclohexanol) propane.

One class of useful epoxy resins are those prepared by condensing epichlorohydrin with bisphenol-A. They include resins represented by the general structural formula (IX):



wherein:

R¹-R⁶ are defined hereinafore, and preferably are all hydrogen;

R²⁰ is independently selected from alkyl radicals, preferably alkyl radicals containing from 1 to 10 carbon atoms, hydroxyl, or halogen radicals;

R²¹ is independently selected from alkyl radicals, preferably alkyl radicals containing from 1 to 10 carbon atoms, hydroxyl, or halogen radicals;

v is independently selected from integers having a value of from 0 to 4 inclusive;

w is independently selected from integers having a value of from 0 to 4 inclusive; and

f has a value of at least one, and varies according to the molecular weight of the resin, with the upper-limit of f preferably not exceeding about 10, more preferably not exceeding about 5.

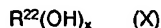
5 Preferred compounds of Formula IX are those wherein $R^1 - R^6$ are all hydrogen, and v and w are all zero.

An example of commercially available and useful epoxy resins are the EPON resins of Shell Oil Company.

As mentioned hereinafore those bis-epoxides, including the epoxy resins, wherein the two carbon atoms of the oxirane ring are bonded to three hydrogen atoms, e.g., wherein $R^1 - R^6$ in Formula V are all hydrogen, are preferred. Preferred bis-epoxides of this type are those wherein the hydrocarbon moieties bridging the epoxide moieties, e.g., R in Formula V, contain polar groups or atoms. These polar groups or atoms include, but are not limited to, the polar hetero atoms or groups described hereinafore. Particularly preferred bis-epoxides are the epoxy resins, especially those devised from polyhydric phenols.

15 In the preferred compositions of the invention, the epoxide equivalent of the epoxide of the polyphenol is preferably limited to a minimum of 145 and a maximum below 250. The epoxide equivalent is defined as the number of grams of material containing one epoxide group. Thus, a suitable starting material is a substance known as Epon 828 which is a commercial epoxidized dihydroxy-di-phenyl-di-methylmethane having an average epoxide equivalent of 175 to 210. Other similar commercial products are available and can be employed as the bis-epoxide. Exemplary of these commercial products are the bis-epoxides of polynuclear phenol. These products for the most part consist principally of the diglycidyl ether of diphenyl-di-methylmethane. The diglycidyl ether of diphenylmono-methylmethane and the diphenylmethane diglycidyl ether can be employed as reactants.

20 The mono- or polyhydric alcohol reactants can comprise at least one member selected from the group consisting of alcohols of the formula:



wherein R^{22} is a hydrocarbyl group or represents a hydrocarbyl chain, optionally containing one or more hetero chain atoms (e.g., O, S or N), and x is a number of from 1 to 8, e.g., 2 to 5 (preferred). Preferred polyhydric alcohols are polyoxyalkylene glycols of the formula:



35 wherein M and T are the same or different and are alkylene groups of at least 2 carbon atoms wherein the sum of y and q is in the range of from 15 to 250, such that the total average molecular weight of the polyoxyalkylene glycol is at least 1,000, preferably from 1,000 to 10,000, more preferably from 2,000 to 8,000. Preferably M and T are either 3 or 4 carbon atoms, and therefore preferably the polyoxyalkylene glycol comprises polypropylene glycol, polybutylene glycol or block copolymer mixtures thereof.

40 The selected polyhydric alcohol and bis-epoxide reactants are contacted for reaction in a weight:weight ratio of polyhydric alcohol to bis-epoxide of from 10:1 to 20:1, preferably from 14:1 to 18:1.

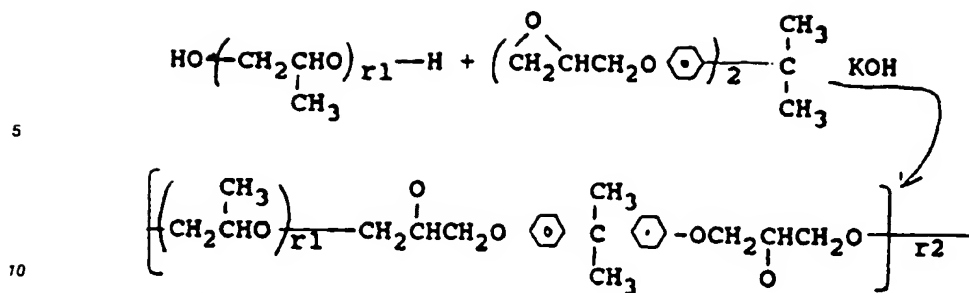
The conditions of reaction in forming the first adduct will vary depending upon such factors as the polyhydric alcohol and bis-epoxide used, the presence of solvent for the reaction and other factors. In general, temperatures within the range of from 110 to 200°C, preferably from 120 to 170°C, will be employed.

45 The reaction for formation of the first adduct may be conducted in the presence of a reaction solvent, such as a hydrocarbon solvent, e.g., toluene, xylene and the like. The quantity of the selected solvent is not critical, although the solvent, e.g., toluene will be usually within the range from 25 to 75 parts of solvent per 100 parts of the first adduct, calculated by weight.

50 The pressure employed in the reaction for formation of the first adduct is not critical, and may be subatmospheric, atmospheric or superatmospheric.

The reaction of the selected polyhydric alcohol and bis-epoxide may be conducted in the presence of a small amount of catalyst for the reaction, such as a Lewis base, e.g., caustic soda or caustic potash, which can be employed in the range of from about 0.2 to 0.5 wt.% of all the components charged to the reaction mixture.

55 The desired adduct formed by the reaction of the polyhydric alcohol and bis-epoxide can be illustrated by reference to the following equation, wherein the reaction of polypropylene glycol and the diglycidyl ether of bis-phenol A is illustrated.



wherein r_1 has the value sufficient to satisfy the number average molecular weight of the polypropylene glycol. For example, r_2 will range generally from about 5 to about 120 for polypropylene glycols having number average molecular weights of from about 4000 to about 7000.

It is not essential that the reaction to form the first adduct be carried to completion and it will be understood that the reaction mass can also contain by-product and unreacted starting material. Illustrative of by-product are dimers, trimers and higher "homologues" formed by reactions of molecules of the selected bis-epoxide with the desired polyhydric alcohol.

The product mixture obtained from preparation of the first adduct can, if desired, be directly charged to a separate reaction vessel for reaction in the second step with the selected amount of the alkylene oxide, e.g., propylene oxide. Alternatively, the alkylene oxide can be directly introduced into the reaction vessel containing the adduct product mixture.

The alkylene oxide reactant for use in the oxyalkylation of the thus-formed bis-epoxide/polyhydric alcohol adduct product mixture comprise alkylene oxides having from 2 to 10, preferably from 2 to 5, carbon atoms provided that the demulsifier prepared therefrom contains at least 40 wt.% of oxyalkylene units derived from alkylene oxides of 3 carbon atoms or greater. Exemplary of such alkylene oxides are ethylene oxide, propylene oxide, 1,2-epoxy butane, 2,3-epoxy butane, 1,2-epoxy pentane, 2,3-epoxy pentane, 1,2-epoxy hexane, 2,3-epoxy hexane, 3,4-epoxy hexane, 1,2-epoxy-3-methyl-butane, and the like. Particularly preferred alkylene oxides are propylene oxide and butylene oxide. Most preferably, the alkylene oxide comprises propylene oxide.

The quantity of the alkylene oxide introduced into the second reaction stage for reaction with the adduct can vary widely, but preferably from 0.1 to 20 parts by weight of alkylene oxide, more preferably from 0.4 to 10 parts by weight of alkylene oxide, and most preferably from 1 to 4 parts by weight of alkylene oxide, are reacted with the adduct product mixture per part by weight of the first adduct product mixture. Preferably, the alkylene oxide charged to this reaction stage will comprise less than about 50 wt.%, still more preferably less than about 40 wt.%, and most preferably less than about 30 wt.% (e.g., 0-20 wt.%), ethylene oxide, with the balance of the charged alkylene oxide comprising propylene oxides and higher epoxides, as described above. The contact of the selected alkylene oxide and the first adduct reaction mixture will be made under conditions for reaction of the alkylene oxide with the hydroxy groups of the first adduct. Conditions effective to achieve such reaction can vary widely, and this second stage reaction will typically employ a reaction temperature within the range of from 110 to 180°C, preferably 130 to 160°C. Any convenient pressure may be used, that is, subatmospheric, atmospheric or superatmospheric, although superatmospheric will be typically preferred.

A mixture of alkylene oxides may be employed, e.g., a mixture of ethylene oxide and a higher alkylene oxide (e.g., propylene oxide or butylene oxide). Alternatively, different alkylene oxides can be charged in any sequence, to form "blocks" of the separately charged alkylene oxide. The order of such sequential oxyalkylation, or the number of repeats of any such oxyalkylation, can be varied widely. For example, the first adduct can be oxyethylated, followed by charging of propylene oxide for oxypropylation, or the first adduct can be first treated with propylene oxide followed by oxyethylation of the oxypropylated adduct. If such sequential alkylations are used with ethylene oxide, propylene or a higher alkylene oxide is preferably charged second (if two alkylation stages are used) or last (in the case of 3 or more alkylation stages), to alkoxyate substantially all of the oxyethylene chain ends.

The reaction of the selected bis-epoxide and polyhydric alcohol, and the alkoxylation of the resulting adduct, are preferably conducted under substantially anhydrous conditions.

The oxyalkylation reaction stage(s) may be conducted in the presence of the Lewis Base catalyst employed in the formation of the first adduct so that it is not necessary to remove the Lewis Base catalyst prior to the introduction of the alkylene oxide. Similarly, the oxyalkylation may be conducted under the

presence of the same or different solvent as employed in the first reaction wherein the first adduct of the bis-epoxide and polyhydric phenol is formed. If desired, additional reaction solvent (e.g., toluene) may be added. The Lewis Base catalyst is preferably neutralized (e.g., by addition of acetic acid or similar alkanolic acid) to a substantially neutral pH (e.g., pH of 5-8).

5 The demulsifiers of this invention will contain at least 40 wt.%, of oxyalkylene units derived from alkylene oxides of 3 carbon atoms or greater (e.g., propylene oxide, butylene oxide, and the like) used in the oxyalkylation step.

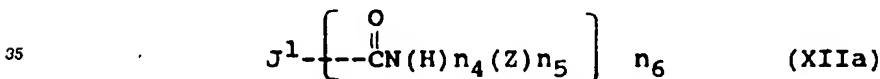
One of the preferred demulsifiers of this invention can be described as the propoxylated copolymer of a diglycidyl ether of bis-phenol A with polypropylene glycol wherein the polypropylene glycol has a molecular weight of from 2000 to 8000, the weight ratio of the polypropylene glycol to the diglycidyl ether of bis-phenol A is within the range of from 14 to 1 to 18 to 1, and the weight ratio of propylene oxide reacted with the first adduct is within the range of from about 2.5:1 to 3.5:1.

COMPATIBILITY ADDITIVE C

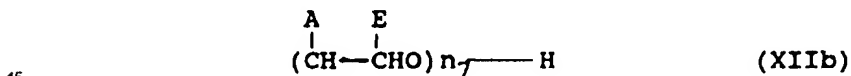
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Preferably, the lubricating oil additive mixtures of this invention further comprise a compatibilizing effective amount of at least one alcohol ester or hydroxyamide derivative of a carboxylic acid having a total of from 24 to 90 carbon atoms and at least 1, e.g., about 2 to 3, carboxylic acid groups per molecule. These ester compatibility additives are derived from the esterification of a monocarboxylic or polycarboxylic acid with a mono-, di- or trihydric alcohol (e.g., glycol, glycerol, oxa-alkane diols). Such esters have been heretofore used in lubricating oils as friction modifiers, and the methods of preparation thereof, and structures, are described in US-A-3,429,817; 4,459,223; 4,479,883; 4,617,026; and 4,683,069. The hydrox-
20 yamide derivatives of such mono- and polycarboxylic acids can be prepared by condensing the acid at elevated temperature with a hydroxyamine (e.g. alkanol amines or aminoalcohols, such as ethanolamine, diethanol-amine, propanolamine, 3-amino-1,1-propanediol), employing the methods disclosed in US-A-
25 4,557,846.

The carboxylic acid may be an aliphatic saturated or unsaturated acid and will generally have a total of 24 to 90, preferably 24 to 60, carbon atoms and at least 1, e.g., 2 to 3, preferably about 2, carboxylic acid groups with at least about 9 carbon atoms, preferably 12 to 42, especially 16 to 22 carbon atoms between
30 the carboxylic acid groups. Exemplary of the hydroxyamide compatibilizers are oil soluble hydroxyamide compounds having the formula:



wherein J¹ is the hydrocarbon radical or skeleton of a dimer carboxylic acid having a total of 24 to 90 carbon atoms with 9 to 42 carbon atoms between carboxylic acid groups; Z is (a) a hydroxy substituted
40 alkyl group having 1 to 20 carbon atoms, or (b) an oxyalkylene group of the formula:



where A and E are each alkyl of 1 to 2 carbon atoms or hydrogen and n₇ is an integer of 1 to 50; n₄ is 0 or 1; n₅ is 1 or 2 and n₆ is 1 or 2.

Preferred compatibilizers comprise partial esters or diesters of dicarboxylic acids of the formulas:

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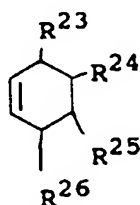
55 wherein J is the hydrocarbon radical of the acid and J' and J'' is either the hydrocarbon radical of an alkane diol or the oxy-alkylene radical from an oxa-alkane diol as defined hereinbelow. Generally 1-3 moles of glycol, preferably 1-2 moles of glycol, are used per mole of acid to provide either a complete or partial ester.

Also, esters can be obtained by esterifying a mono- or dicarboxylic acid or mixture of such acids with a mixture of diols, in which case J would then be the hydrocarbon radical of the dicarboxylic acid(s) and J' and J'' would be the hydrocarbon radicals associated with the diols.

The compatibility additives are used in amounts ranging from 0.1 to 5 parts by weight, more preferably 0.5 to 1.5 parts by weight based upon the weight of the Component B demulsifier additive in the lubricating oil composition. If desired, higher amounts of the compatibility additive may be employed, since such polycarboxylic acid-glycol esters may also serve as friction modifiers in the lubricating oil composition. Therefore, the compatibility additives will be generally employed in an amount of from 0.0005 to 2, more preferably from 0.001 to 0.25, and most preferably from 0.005 to 0.1, weight percent.

Especially preferred compatibilizer additives are the dimer acid esters. The term dimer acid used herein is meant to refer to those substituted cyclohexene dicarboxylic acids formed by a Diels-Alder-type reaction (which is a thermal condensation) of C₁₈-C₂₂ unsaturated fatty acids, such as tall oil fatty acids, which typically contain 85 to 90 percent oleic or linoleic acids. Such dimer acids typically contain 36 carbon atoms. The dimer acid structure can be generalized as follows:

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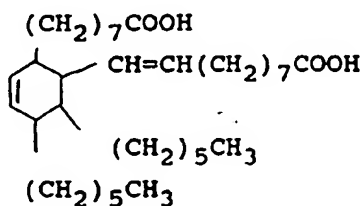


(XIV)

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with two of the R²³-R²⁶ groups containing carboxyl groups and two being hydrocarbon groups depending upon how the condensation of the carboxylic acid has occurred. The carboxyl groups can be -(CH₂)₈COOH; -CH=CH(CH₂)₈COOH; -(CH₂)₇COOH; -CH₂-CH=CH(CH₂)₇COOH; -CH=CH(CH₂)₇COOH and the hydrocarbon terminating group can be represented by: CH₃(CH₂)₄-; CH₃(CH₂)₅-; CH₃(CH₂)₇-; CH₃(CH₂)₄CH=CH-; CH₃(CH₂)₄CH=CHCH₂-, and the like. The dimer of linoleic acid which is the preferred embodiment can be expressed in the following formula:

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(XV)

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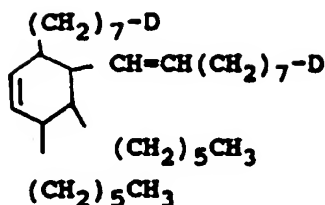
Also the term dimer acid as used herein necessarily includes products containing trimers (and higher homologues), e.g., up to about 24 percent by weight trimer, but more typically about 10 percent by weight trimer since, as is well known in the art, the dimerization reaction provides a product containing a trimer acid having molecular weight of about three times the molecular weight to the starting fatty acid.

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The polycarboxylic acids or dimer acids noted above are esterified with a glycol, the glycol being an alkane diol or oxa-alkane diol represented by the formula HO(R²⁷CHCH₂O)_xH wherein R²⁷ is H or CH₃ and x¹ is 1 to 100, preferably 1 to 25 with ethylene glycol and diethylene glycol particularly preferred. A preferred embodiment is formation of the ester with 1 to 2 moles of glycol per mole of dimer acid or polycarboxylic acid, such as the ester of diethylene glycol with dimerized linoleic acid. Illustrative of such esters are compounds of the formula (XVI):

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wherein D is



x^1 is as defined above.

The preparation and use of the foregoing polycarboxylic acid glycol esters as friction reducing esters (viz., friction modifiers) is disclosed in US-A-4,505,829.

METAL DETERGENT COMPONENT D

The lubricating oil metal detergent additives are also frequently referred to as rust inhibitors and include the magnesium or calcium or barium salts of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylates and naphthenates. Highly basic, that is overbased metal salts, are frequently used as detergents and appear particularly prone to interaction with the ashless dispersant. Usually these metal containing rust inhibitors and detergents are used in lubricating oil in amounts of 0.01 to 10, e.g. 0.1 to 5 wt. %, based on the weight of the total lubricating composition. Marine diesel lubricating oils typically employ such metal-containing rust inhibitors and detergents in amounts of up to about 20 wt. %.

Highly basic alkaline earth metal sulfonates are frequently used as detergents. They are usually produced by heating a mixture comprising an oil-soluble sulfonate or alkaryl sulfonic acid, with an excess of alkaline earth metal compound above that required for complete neutralization of any sulfonic acid present and thereafter forming a dispersed carbonate complex by reacting the excess metal with carbon dioxide to provide the desired overbasing. The sulfonic acids are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum by distillation and/or extraction or by the alkylation of aromatic hydrocarbons as for example those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl and the halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from 3 to more than 30 carbon atoms. For example haloparaffins, olefins obtained by dehydrogenation of paraffins, polyolefins produced from ethylene, propylene, are all suitable. The alkaryl sulfonates usually contain from 9 to 70 or more carbon atoms, preferably from 16 to 50 carbon atoms per alkyl substituted aromatic moiety.

The alkaline earth metal compounds which may be used in neutralizing these alkaryl sulfonic acids to provide the sulfonates includes the oxides and hydroxides, alkoxides, carbonates, carboxylate, sulfide, hydrosulfide, nitrate, borates and ethers of magnesium, calcium, and barium. Examples are calcium oxide, calcium hydroxide, magnesium acetate and magnesium borate. As noted, the alkaline earth metal compound is used in excess of that required to complete neutralization of the alkaryl sulfonic acids. Generally, the amount ranges from about 100 to 220%, although it is preferred to use at least 125%, of the stoichiometric amount of metal required for complete neutralization.

Various other preparations of basic alkaline earth metal alkaryl sulfonates are known, such as US-A-3,150,088 and 3,150,089 wherein overbasing is accomplished by hydrolysis of an alkoxide-carbonate complex with the alkaryl sulfonate in a hydrocarbon solvent-diluent oil.

A preferred alkaline earth sulfonate additive is magnesium alkyl aromatic sulfonate having a total base number ASTM D2896 ranging from 300 to 400 with the magnesium sulfonate content ranging from 25 to 32 wt. %, based upon the total weight of the additive system dispersed in mineral lubricating oil.

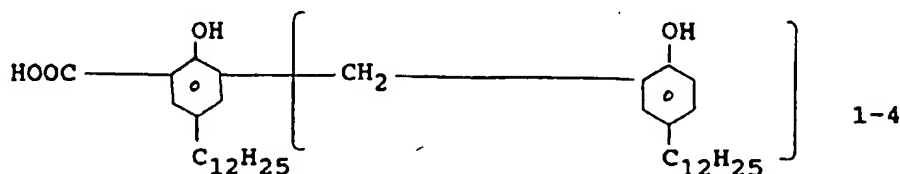
Neutral metal sulfonates are frequently used as rust inhibitors. Polyvalent metal alkyl salicylate and naphthenate materials are known additives for lubricating oil compositions to improve their high temperature

performance and to counteract deposition of carbonaceous matter on pistons (US-A-2,744,069). An increase in reserve basicity of the polyvalent metal alkyl salicylates and naphthenates can be realized by utilizing alkaline earth metal, e.g. calcium, salts of mixtures of C₈-C₂₆ alkyl salicylates and phenates (see US-A-2,744,069) or polyvalent metal salts of alkyl salicylic acids, said acids obtained from the alkylation of phenols followed by phenation, carboxylation and hydrolysis (US-A-3,704,315) which could then be converted into highly basic salts by techniques generally known and used for such conversion. The reserve basicity of these metal-containing rust inhibitors is usefully at TBN levels of between 60 and 150. Included with the useful polyvalent metal salicylate and naphthenate materials are the methylene and sulfur bridged materials which are readily derived from alkyl substituted salicylic or naphthenic acids or mixtures of either or both with alkyl substituted phenols. Basic sulfurized salicylates and a method for their preparation is shown in US-A-3,595,791. Such materials include alkaline earth metal, particularly magnesium, calcium, strontium and barium salts of aromatic acids having the general formula:



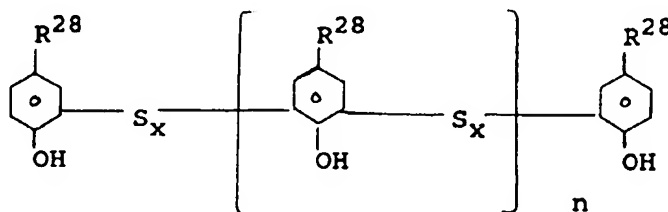
where Ar is an aryl radical of 1 to 6 rings, R₁ is an alkyl group having from 8 to 50 carbon atoms, preferably 12 to 30 carbon atoms (optimally about 12), X is a sulfur (-S-) or methylene (-CH₂-) bridge, y is a number from 0 to 4 and n is a number from 0 to 4.

Preparation of the overbased methylene bridged salicylate-phenate salt is readily carried out by conventional techniques such as by alkylation of a phenol followed by phenation, carboxylation, hydrolysis, methylene bridging a coupling agent such as an alkylene dihalide followed by salt formation concurrent with carbonation. An overbased calcium salt of a methylene bridged phenol-salicylic acid of the general formula (XVIII):



with a TBN of 60 to 150 is highly useful in this invention.

The sulfurized metal phenates can be considered the "metal salt of a phenol sulfide" which thus refers to a metal salt whether neutral or basic, of a compound typified by the general formula (XIX):



where x = 1 or 2, n = 0, 1 or 2; or a polymeric form of such a compound, where R²⁸ is an alkyl radical, n and x are each integers from 1 to 4, and the average number of carbon atoms in all of the R²⁸ groups is at least about 9 in order to ensure adequate solubility in oil. The individual R²⁸ groups may each contain from 5 to 40, preferably 8 to 20, carbon atoms. The metal salt is prepared by reacting an alkyl phenol sulfide with a sufficient quantity of metal containing material to impart the desired alkalinity to the sulfurized metal phenate.

Regardless of the manner in which they are prepared, the sulfurized alkyl phenols which are useful generally contain from 2 to 14% by weight, preferably 4 to 12 wt. % sulfur based on the weight of sulfurized alkyl phenol.

The sulfurized alkyl phenol may be converted by reaction with a metal containing material including oxides, hydroxides and complexes in an amount sufficient to neutralize said phenol and, if desired, to overbase the product to a desired alkalinity by procedures well known in the art. Preferred is a process of neutralization utilizing a solution of metal in a glycol ether.

The lubricating oil additive mixtures of the present invention can be incorporated into a lubricating oil in any convenient way. Thus, these mixtures can be added directly to the oil by dispersing or dissolving the same in the oil at the desired level of concentrations of the ashless dispersant, demulsifier, compatibility additive, and metal detergent (where employed), respectively. Such blending into the additional lube oil can occur at room temperature or elevated temperatures. Alternatively, the ashless dispersant, demulsifier, compatibility additive, and metal detergent (where employed) can be blended with a suitable oil-soluble solvent or base oil to form a concentrate, and which can then be blended with a lubricating oil basestock to obtain the final formulation. Such concentrates will typically contain (on an active ingredient (A.I.) basis) from 3 to 45 wt. %, and preferably from 10 to 35 wt. %, ashless dispersant additive A; typically from 0.01 to 3 wt.%, and preferably from 0.05 to 0.3 wt.% demulsifier additive B; (where present) typically from 0.0005 to 2 wt.%, preferably from 0.001 to 0.25 wt.%, and most preferably from 0.005 to 0.1 wt.% compatibility additive C; (where present) typically from 2 to 45 wt.%, and preferably from 2 to 14 wt.%, metal detergent D; and typically from 30 to 90 wt. %, preferably from 40 to 60 wt. %, base oil, based on the concentrate weight.

Additive packages i.e. concentrates of this invention comprising ashless dispersant, metal detergent, demulsifier and compatibility additive (alone or together with other lubricating oil additives as discussed below, e.g., antiwear additives, corrosion inhibitors, antioxidants, etc.) are preferably prepared in the following manner. The ashless dispersant and metal detergent components (in the selected baseoil or solvent) are preferably first blended together at elevated temperature (e.g., from 70 to 130 °C) for a time and under stirring sufficient to intimately contact these components, followed by cooling of the dispersant/detergent mixture to 65 °C or below, as disclosed in co-pending EP-A-0294-096. The selected demulsifier and compatibility additive are separately admixed in the selected baseoil or solvent for a time and under conditions sufficient to intimately contact these components (e.g., from 50 to 130 °C, for 1 to 5 hours, with stirring), and then introduced as a mixture to the dispersant/detergent mixture, e.g., at 50 to 130 °C with stirring to provide intimate blending, for 1 to 5 hours. The remaining lubricating oil additives can be added (separately or simultaneously) prior to, during or after the mixing of the dispersant/detergent mixture with the demulsifier/compatibility additive mixture.

The lubricating oil basestock for the lubricating oil mixture typically is adapted to perform a selected function by the incorporation of additional additives therein to form lubricating oil compositions (i.e., formulations).

LUBRICATING COMPOSITIONS

The additive mixtures of the present invention possess very good demulsifying properties as measured herein in a wide variety of environments. Accordingly, the additive mixtures are used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additive mixtures of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from 65 ° to 430 °C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from 0.001 to 0.5, and preferably 0.005 to 0.15 weight percent, based on the total weight of the composition, will usually be employed.

The additive mixtures of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additive mixtures of the present invention.

These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers, antioxidants, corrosion inhibitors, detergents, dispersants, pour point depressants, antiwear agents, friction modifiers, etc.

In the preparation of lubricating oil formulations it is common practice to introduce the additives in the form of 10 to 80 wt. %, e.g., 20 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Usually these concentrates may be diluted with 3 to 100, e.g. 5 to

40 parts by weight of lubricating oil, per part by weight of the additive package, in forming finished lubricants, e.g. crankcase motor oils. The purpose of concentrates, of course, is to make the handling of the various materials less difficult and awkward as well as to facilitate solution or dispersion in the final blend. Thus, a metal hydrocarbyl sulfonate or a metal alkyl phenate would be usually employed in the form of a 40 to 50 wt. % concentrate, for example, in a lubricating oil fraction.

The ashless dispersant and demulsifier mixtures of the present invention, alone or with compatibilizer and metal detergent (where present), will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof.

Natural base oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butylphenyl)silicate, hexa-(4-methyl-2-pentoxyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The ashless dispersant demulsifier mixtures of the present invention can also be used with V.I improvers to form multi-grade automobile engine lubricating oil formulations. Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10³ to 10⁶, preferably 10⁴ to 10⁵, e.g., 20,000 to 250,000, as determined by gel permeation chromatography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more monomers of C_2 to C_{30} , e.g. C_2 to C_8 olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, cycloaliphatic, etc. Frequently they will be of ethylene with C_3 to C_{30} olefins, particularly preferred being the copolymers of ethylene and propylene.

5 Other polymers can be used such as polyisobutylenes, homopolymers and copolymers of C_6 and higher alpha olefins, atactic polypropylene, hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof. The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and it may be oxidized and contain oxygen.

10 The preferred hydrocarbon polymers are ethylene copolymers containing from 15 to 90 wt. % ethylene, preferably 30 to 80 wt. % of ethylene and 10 to 85 wt. %, preferably 20 to 70 wt. % of one or more C_3 to C_{28} , preferably C_3 to C_{18} , more preferably C_3 to C_8 , alpha-olefins. While not essential, such copolymers preferably have a degree of crystallinity of less than 25 wt. %, as determined by X-ray and differential scanning calorimetry. Copolymers of ethylene and propylene are most preferred. Other alpha-olefins
15 suitable in place of propylene to form the copolymer, or to be used in combination with ethylene and propylene, to form a terpolymer, tetrapolymer, include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc.; also branched chain alpha-olefins, such as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methylpentene-1, 4,4-dimethyl-1-pentene, and 6-methylheptene-1, and mixtures thereof.

Terpolymers, tetrapolymers, etc., of ethylene, said C_3 - C_{28} alpha-olefin, and a non-conjugated diolefin or
20 mixtures of such diolefins may also be used. The amount of the non-conjugated diolefin generally ranges from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent, based on the total amount of ethylene and alpha-olefin present.

The polyester V.I. improvers are generally polymers of esters of ethylenically unsaturated C_3 to C_8 mono- and dicarboxylic acids such as methacrylic and acrylic acids, maleic acid, maleic anhydride, fumaric
25 acid.

Examples of unsaturated esters that may be used include those of aliphatic saturated mono alcohols of at least 1 carbon atom and preferably of from 12 to 20 carbon atoms, such as decyl acrylate, lauryl acrylate, stearyl acrylate, eicosanyl acrylate, docosanyl acrylate, decyl methacrylate, diamyl fumarate, lauryl methacrylate, cetyl methacrylate, stearyl methacrylate, and the like and mixtures thereof.

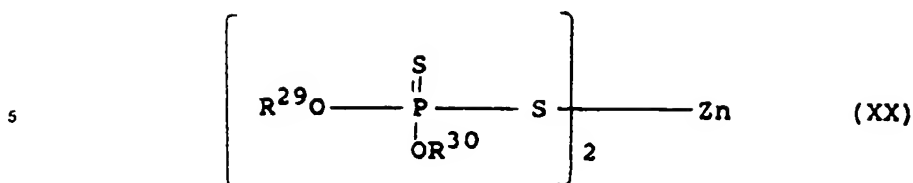
30 Other esters include the vinyl alcohol esters of C_2 to C_{22} fatty or mono carboxylic acids, preferably saturated such as vinyl acetate, vinyl laurate, vinyl palmitate, vinyl stearate, vinyl oleate, and the like and mixtures thereof. Copolymers of vinyl alcohol esters with unsaturated acid esters such as the copolymer of vinyl acetate with dialkyl fumarates, can also be used.

The esters may be copolymerized with still other unsaturated monomers such as olefins, e.g. 0.2 to 5
35 moles of C_2 - C_{20} aliphatic or aromatic olefin per mole of unsaturated ester, or per mole of unsaturated acid or anhydride followed by esterification. For example, copolymers of styrene with maleic anhydride esterified with alcohols and reacted with amines are known, e.g., see US-A-3,702,300.

Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear agents and also provide antioxidant activity. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10,
40 preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P_2S_5 and then neutralizing the dithiophosphoric acid with a suitable zinc compound.

Mixtures of alcohols may be used including mixtures of primary and secondary alcohols, secondary
45 generally for imparting improved anti-wear properties, with primary giving improved thermal stability properties. Mixtures of the two are particularly useful. In general, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

50 The zinc dihydrocarbyl dithiophosphates useful in the present invention are oil soluble salts of dihydrocarbyl esters of dithiophosphoric acids and may be represented by the following formula:



wherein R^{29} and R^{30} may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^{29} and R^{30} groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R^{29} and R^{30} in formula XX) in the dithiophosphoric acid will generally be about 5 or greater.

The antioxidants useful in this invention include copper compounds. A copper compound may be blended into the oil (e.g., an oil soluble copper compound) to provide copper in an oil-solubilized form. By oil soluble we mean the compound is oil soluble under normal blending conditions in the oil or additive package. The copper compound may be in the cuprous or cupric form. The copper may be in the form of the copper dihydrocarbyl thio- or dithio-phosphates wherein copper may be substituted for zinc in the compounds and reactions described above although one mole of cuprous or cupric oxide may be reacted with one or two moles of the dithiophosphoric acid, respectively. Alternatively the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples include C_{10} to C_{18} fatty acids such as stearic or palmitic, but unsaturated acids such as oleic or branched carboxylic acids such as naphthenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil soluble copper dithiocarbamates of the general formula $(\text{R}^{31}\text{R}^{32}\text{NCSS})_n\text{Cu}$, where n is 1 or 2 and R^{31} and R^{32} are the same or different hydrocarbyl radicals containing from 1 to 18 and preferably 2 to 12 carbon atoms and including radicals such as alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^{31} and R^{32} groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-heptyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl, etc. In order to obtain oil solubility, the total number of carbon atoms (i.e. R^{31} and R^{32}) will generally be about 5 or greater. Copper sulphonates, phenates, and acetylacetonates may also be used.

Exemplary of useful copper compounds are copper (Cu^I and/or Cu^{II}) salts of alkenyl succinic acids or anhydrides. The salts themselves may be basic, neutral or acidic. They may be formed by reacting (a) any of the materials discussed above in the Ashless Dispersant section, which have at least one free carboxylic acid (or anhydride) group with (b) a reactive metal compound. Suitable acid (or anhydride) reactive metal compounds include those such as cupric or cuprous hydroxides, oxides, acetates, borates, and carbonates or basic copper carbonate.

Examples of the metal salts of this invention are Cu salts of polyisobutenyl succinic anhydride (hereinafter referred to as Cu-PIBSA), and Cu salts of polyisobutenyl succinic acid. Preferably, the selected metal employed is its divalent form, e.g., Cu^{+2} . The preferred substrates are polyalkenyl succinic acids in which the alkenyl group has a molecular weight greater than about 700. The alkenyl group desirably has a \overline{M}_n from 900 to 1400, and up to 2500, with a \overline{M}_n of about 950 being most preferred. Especially preferred, of those listed above in the section on Dispersants, is polyisobutylene succinic acid (PIBSA). These materials may desirably be dissolved in a solvent, such as a mineral oil, and heated in the presence of a water solution (or slurry) of the metal bearing material. Heating may take place between 70° and 200°C . Temperatures of 110° to 140°C are entirely adequate. It may be necessary, depending upon the salt produced, not to allow the reaction to remain at a temperature above about 140°C for an extended period of time, e.g., longer than 5 hours, or decomposition of the salt may occur.

The copper antioxidants (e.g., Cu-PIBSA, Cu-oleate, or mixtures thereof) will be generally employed in an amount of from 50-500 ppm by weight of the metal, in the final lubricating or fuel composition.

The copper antioxidants used in this invention are inexpensive and are effective at low concentrations and therefore do not add substantially to the cost of the product. The results obtained are frequently better than those obtained with previously used antioxidants, which are expensive and used in higher concentrations. In the amounts employed, the copper compounds do not interfere with the performance of other

components of the lubricating composition, in many instances, completely satisfactory results are obtained when the copper compound is the sole antioxidant in addition to the ZDDP. The copper compounds can be utilized to replace part or all of the need for supplementary antioxidants. Thus, for particularly severe conditions it may be desirable to include a supplementary, conventional antioxidant. However, the amounts of supplementary antioxidant required are small, far less than the amount required in the absence of the copper compound.

While any effective amount of the copper antioxidant can be incorporated into the lubricating oil composition, it is contemplated that such effective amounts be sufficient to provide said lube oil composition with an amount of the copper antioxidant of from 5 to 500 (more preferably 10 to 200, still more preferably 10 to 180, and most preferably 20 to 130 (e.g., 90 to 120)) part per million of added copper based on the weight of the lubricating oil composition. Of course, the preferred amount may depend amongst other factors on the quality of the basestock lubricating oil.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 1/2 to 15 hours, at a temperature in the range of 65° to 315°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in US-A-1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids.

Representative examples of suitable friction modifiers are found in US-A-3,933,659 which discloses fatty acid esters and amides; US-A-4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; US-A-4,105,571 which discloses glycerol esters of dimerized fatty acids; US-A-3,779,928 which discloses alkane phosphonic acid salts; US-A-3,778,375 which discloses reaction products of a phosphonate with an oleamide; US-A-3,852,205 which discloses S-carboxy-alkylene hydrocarbyl succinimide, S-carboxy-alkylene hydrocarbyl succinamic acid and mixtures thereof; US-A-3,879,306 which discloses N-(hydroxyalkyl) alkenyl-succinamic acids or succinimides; US-A-3,932,290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and US-A-4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. The most preferred friction modifiers are glycerol mono and dioleates, and succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols such as described in US-A-4,344,853.

Pour point depressants lower the temperature at which the fluid will flow or can be poured. Such depressants are well known. Typical of those additives which usefully optimize the low temperature fluidity of the fluid are C₈-C₁₈ dialkylfumarate vinyl acetate copolymers, polymethacrylates, and wax naphthalene.

Foam control can be provided by an antifoamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane.

Organic, oil-soluble compounds useful as rust inhibitors in this invention comprise nonionic surfactants such as polyoxyalkylene polyols and esters thereof, and anionic surfactants such as salts of alkyl sulfonic acids. Such anti-rust compounds are known and can be made by conventional means. Nonionic surfactants, useful as anti-rust additives in the oleaginous compositions of this invention, usually owe their surfactant properties to a number of weak stabilizing groups such as ether linkages. Nonionic anti-rust agents containing ether linkages can be made by alkoxyating organic substrates containing active hydrogens with an excess of the lower alkylene oxides (such as ethylene and propylene oxides) until the desired number of alkoxy groups have been placed in the molecule.

The preferred rust inhibitors are polyoxyalkylene polyols and derivatives thereof. This class of materials are commercially available from various sources: Pluronic Polyols from Wyandotte Chemicals Corporation; Polyglycol 112-2, a liquid triol derived from ethylene oxide and propylene oxide available from Dow Chemical Co.; and Tergitol, dodecylphenyl or monophenyl polyethylene glycol ethers, and Ucon, polyalkylene glycols and derivatives, both available from Union Carbide Corp. These are but a few of the

commercial products suitable as rust inhibitors in the improved composition of the present invention.

In addition to the polyols per se, the esters thereof obtained by reacting the polyols with various carboxylic acids are also suitable. Acids useful in preparing these esters are lauric acid, stearic acid, succinic acid, and alkyl- or alkenyl-substituted succinic acids wherein the alkyl- or alkenyl group contains up to about

5 twenty carbon atoms.

The preferred polyols are prepared as block polymers. Thus, a hydroxy-substituted compound, $Q-(OH)_{n_8}$ (wherein n_8 is 1 to 6, and Q is the residue of a mono- or polyhydric alcohol, phenol, naphthol, etc.) is reacted with propylene oxide to form a hydrophobic base. This base is then reacted with ethylene oxide to provide a hydrophilic portion resulting in a molecule having both hydrophobic and hydrophilic portions. The

10 relative sizes of these portions can be adjusted by regulating the ratio of reactants, time of reaction, as is obvious to those skilled in the art. Thus it is within the skill of the art to prepare polyols whose molecules are characterized by hydrophobic and hydrophilic moieties which are present in a ratio rendering rust inhibitors suitable for use in any lubricant composition regardless of differences in the base oils and the presence of other additives.

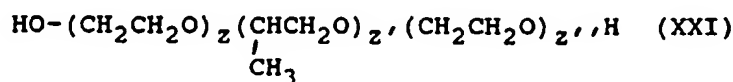
15 If more oil-solubility is needed in a given lubricating composition, the hydrophobic portion can be increased and/or the hydrophilic portion decreased. If greater oil-in-water emulsion breaking ability is required, the hydrophilic and/or hydrophobic portions can be adjusted to accomplish this.

Compounds illustrative of $Q-(OH)_{n_8}$ include alkylene polyols such as the alkylene glycols, alkylene triols, alkylene tetrols, etc., such as ethylene glycol, propylene glycol, glycerol, pentaerythritol, sorbitol, 20 mannitol, and the like. Aromatic hydroxy compounds such as alkylated mono- and polyhydric phenols and naphthols can also be used, e.g., heptylphenol, dodecylphenol.

Other suitable demulsifiers include the esters disclosed in US-A-3,098,827 and 2,674,619.

The liquid polyols available from Wyandotte Chemical Co. under the name Pluronic Polyols and other similar polyols are particularly well suited as rust inhibitors. These Pluronic Polyols correspond to the

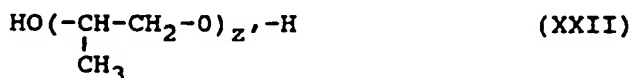
25 formula:



30

wherein z , z' and z'' are integers greater than 1 such that the $-CH_2CH_2O-$ groups comprise from 10% to 40% by weight of the total molecular weight of the glycol, the average molecule weight of said glycol being from 1000 to 5000. These products are prepared by first condensing propylene oxide with propylene glycol

35 to produce the hydrophobic base



40

This condensation product is then treated with ethylene oxide to add hydrophilic portions to both ends of the molecule. For best results, the ethylene oxide units should comprise from 10 to 40% by weight of the molecule. Those products wherein the molecular weight of the polyol is from 2500 to 4500 and the ethylene

45 oxide units comprise from 10% to 15% by weight of the molecule are particularly suitable. The polyols having a molecular weight of 4000 with about 10% attributable to (CH_2CH_2O) units are particularly good. Also useful are alkoxyated fatty amines, amides, alcohols and the like, including such alkoxyated fatty acid derivatives treated with C_9 to C_{16} alkyl-substituted phenols (such as the mono- and di-heptyl, octyl, nonyl, decyl, undecyl, dodecyl and tridecyl phenols), as described in US-A-3,849,501.

50 These compositions of our invention may also contain other additives such as those previously described, and other metal containing additives, for example, those containing barium and sodium.

The lubricating composition of the present invention may also include copper lead bearing corrosion inhibitors. Typically such compounds are the thiadiazole polysulphides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Preferred materials are the derivatives of 1,3,4 thiadiazoles

55 such as those described in US-A-2,719,125; 2,719,126; and 3,087,932; especially preferred is the compound 2,5 bis (t-octadithio)-1,3,4 thiadiazole commercially available as Amoco 150. Other similar materials also suitable are described in US-A-3,821,236; 3,904,537; 4,097,387; 4,107,059; 4,136,043; 4,188,299; and 4,193,882.

Other suitable additives are the thio and polythio sulphenamides of thiadiazoles such as those described in GB-A-1,560,830. When these compounds are included in the lubricating composition, we prefer that they be present in an amount from 0.01 to 10, preferably 0.1 to 5.0 weight percent based on the weight of the composition.

5 Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

Compositions when containing these conventional additives are typically blended into the base oil in amounts effective to provide their normal attendant function. Representative effective amounts of such additives (as the respective active ingredients) in the fully formulated oil are illustrated as follows:

10

Compositions	Wt.% A.I. (Preferred)	Wt.% A.I. (Broad)
Ashless Dispersant (Component A)	0.1- 8	0.1-20
Polymeric Viscosity Index Improver (Component A)	0.01-2	0.001-10
15 Demulsifier (Component B)	0.001-0.03	0.001-0.3
Compatibilizer (Component C)	0.001-0.25	0.0005-2
Metal Detergents (Component D)	0.01-3	0.01-20
Viscosity Modifier	0.01-4	0.01-12
Corrosion Inhibitor	0.01-1.5	0.01-5
20 Oxidation Inhibitor	0.01-1.5	0.01-5
Pour Point Depressant	0.01-1.5	0.01-5
Anti-Foaming Agents	0.001-0.15	0.001-3
Anti-Wear Agents	0.001-1.5	0.001-5
Friction Modifiers	0.01-1.5	0.01-5
25 Mineral Oil Base	Balance	Balance

When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the novel ashless dispersant/demulsifier mixtures of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (including metal detergent, compatibilizer, etc.) (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition or formulation. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The concentrate or additive-package will typically be formulated to contain the additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base lubricant. Thus, the mixtures of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from 2.5 to 90%, and preferably from 15 to 75%, and most preferably from 25 to 60% by weight additives in the appropriate proportions with the remainder being base oil.

The final formulations may employ typically about 10 wt. % of the additive-package with the remainder being base oil.

All of said weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted and which include preferred embodiments of the invention.

50 EXAMPLES

A series of test lubricating oil formulations are prepared containing ashless dispersant, metal detergent, viscosity modifier and the demulsifiers of this invention, or other test materials, identified in Tables I and II below. To measure the crankcase pressure generated, the indicated compositions were tested in a shortened version of the Sequence IID test (referred to as the IID Screener) in which the ASTM Sequence IID procedure is followed for 12 hours using an Oldsmobile V8 engine which is not rebuilt but is instead carefully flushed between runs. Crankcase pressure is monitored for the 12 hours to produce an integrated (cumulative) crankcase pressure value. The data thereby obtained are summarized in Table III. This test can thus be used to predict tendency of lubricants to form emulsions and generate crankcase pressure in the

Sequence IID.

Table I

Formulations	
Component	(Wt.% a.i.)
Ashless dispersant ⁽¹⁾	3.0
Metal detergent ⁽²⁾	0.74
Demulsifier	(See Table III)
Base oil ⁽³⁾	Balance

Notes:

(1) Borated polyisobutenyl (PIB \overline{M}_n = 2200) succinimide of polyethylene polyamine.

(2) Overbased magnesium sulfonate detergent, TBN = 400.

(3) Solvent (about 130) Neutral mineral baseoil, also containing copper antioxidant, zinc dialkyl dithiophosphate antiwear agent, and ethylene-propylene copolymer viscosity index improver.

Table II

Demulsifier			
Example No.	Demulsifier(1)	EO:PO Wt. Ratio(2)	Alkylene Oxide:Adduct Wt.Ratio(3)
1	Propoxylated adduct of polypropylene glycol and diglycidyl ether of bis-phenol A	0:100	3:1
2	Propoxylated adduct of polypropylene glycol and diglycidyl ether of bis-phenol A	0:100	0.6:1
3	Ethoxylated propoxylated adduct of polypropylene glycol and diglycidyl ether of bis-phenol A	30:70	0.6:1

Notes:

(1) Polypropylene glycol, Average Mol.Wt. = 5000.

(2) EO = ethylene oxide; PO = propylene oxide; wt. ratio based on ethylene oxide and propylene oxide reacted with polypropylene glycol/diglycidyl ether of bis-phenol A adduct ("adduct").

(3) Alkylene oxide:adduct ratio based on weight of alkylene oxide and adduct charged.

Table III

Example No.	Demulsifier	Demulsifier		Integrated Crankcase Pressure Units
		(Wt.%)	(wppm)	
4	Prepared as in Example 1	0.01	100	21.2
5	Prepared as in Example 1	0.015	150	5.8
6	Prepared as in Example 1	0.02	200	6.0
7	Prepared as in Example 1	0.05	500	4.0
8	Prepared as in Example 2	0.02	200	18.3
9	Prepared as in Example 2	0.05	500	4.7
10	Prepared as in Example 2	0.15	1,500	21.0
11	Prepared as in Example 3	0.05	500	47.2
Comp.A	Polypropylene glycol ⁽¹⁾	0.015	150	97.3
Comp.B	Polypropylene glycol/diglycidyl ether adduct ⁽²⁾	0.015	150	82.4
Comp.C ⁽³⁾	None	-	-	112.4

Notes:

(1) Corresponds to the polypropylene glycol used as feed to Example 1.

(2) Prepared as in Example 1(a).

(3) Composition as in Table I with no added demulsifier.

The pressure data in Table III indicate the surprisingly reduced crankcase pressure resulting from the use of the demulsifiers of this invention in Examples 4-11 as compared to the polypropylene glycol and polypropylene glycol/diglycidyl ether adduct in Comparative Examples A and B, respectively, and as compared to the much higher crankcase pressure generated by the control, non-demulsified control (Comparative Example C). The propoxylated demulsifiers of Examples 1 - 2 provided particularly reduced crankcase pressure, and were superior in this respect to the demulsifier of Example 3 which contained equal weights of oxyalkylene units derived from ethylene oxide and propylene oxide. Comparative B illustrates the criticality to the alkoxylation step in preparing the demulsifiers of this invention.

While not wishing to be bound thereby, it is believed that the alkoxylation step serves both to chain extend the bis-epoxide/polyhydric alcohol adduct by the addition of oxyalkylene moieties to chain ends of the adduct, and to alkoxyate hydroxy groups in the adduct which are formed by ring opening of the epoxy groups of the bis-epoxide, but some of which are not further reacted during the adduct preparation stage.

EXAMPLES 12-18

In a separate series of tests, additive packages for crankcase lubricating oils were prepared having the following components identified in Table IV. Each additive package was stored at 66°C and observed to determine the onset of any formation of haze, an indication of additive package stability. The data thereby obtained are summarized in Table V below:

Table IV

Additive Concentrates	
Component	Wt.% (a.i.)
Ashless dispersant(1)	26-27
Metal detergent(2)	6-7
Demulsifier	(see Table V)
Compatibility additive(3)	0, 0.5, 1.0
Base oil(4)	Balance

Notes:

(1) Polyisobutenyl (PIB $\overline{M}_n = 2200$) succinimide of polyethylene polyamine.

(2) Overbased Mg sulfonate detergent (TBN = 400).

(3) Diethylene glycol ester of dimer and trimer of linoleic acid.

(4) Solvent (about 150) neutral mineral oil base oil, also containing copper antioxidant, zinc dialkyldithiophosphate antiwear agent, ethylene propylene copolymer viscosity index improver and supplemental nonylphenol sulfide antioxidant.

Table V

Example No.	Demulsifier Prepared as in Example:		Compatibility Additive (wt.%)	Adpack Stability at 66°C	
	Prepared as in Example:	(Wt.%)		No. Days	Appearance
12	2	1	None	5	haze
13	2	1	1.0	96	ok
14	1	1	None	5	haze
15	1	1	1.0	5 33	slight haze haze
16	1	0.3	None	4 39	slight haze haze
17	1	0.3	0.5	95	ok
18	1	0.3	1.0	95	ok

The data in Table V illustrate the improved additive package stability observed in use of the demulsifiers and compatibility additives of this invention. Substantial improvements in reduced haze were achieved when the propoxylated demulsifier of Example 2, wherein a propylene oxide:adduct weight:weight ratio of 0.6:1 was employed, in combination with a compatibility additive of this invention. Whereas haze was observed after 5 days in Example 12, no haze appeared in the additive package of Example 13 even after 96 days of storage at 66°C. Similar improvements in the haze appearance using the propoxylated demulsifier of Example 1, having a PO:adduct ratio of 3:1, in combination with a compatibility additive of this invention, as may be seen by comparing Example 15 to the additive package of Example 14, wherein a

compatibility additive was not employed, and by comparing Examples 17 and 18 (employing varying amounts of the compatibility additive), to the additive package of Example 16.

EXAMPLES 19-24.

5

In separate runs, a series of lubricating oil concentrates ("additive packages") are prepared by blending 10 parts of S150N lubricating oil, 55 parts of an ashless dispersant (polyisobutennyl succinimide of a polyethylene polyamine having about 7 carbon atoms and 5 to 6 nitrogen atoms per polyamine molecule) and 11 parts of metal detergent additive (overbased Mg sulfonate, TBN = 400), for 3 hours at a
10 temperature of 100°C. Aliquots of each blend are then taken and are observed to be clear of any visible haze or sediment.

The temperature of each blend is cooled to 75°C, and then the following additional components are introduced, with the indicated components being used in the same concentrations in each blend: zinc dialkyl dithiophosphate antiwear agent, nonyl phenol sulfide oxidation inhibitor, and copper antioxidant, to
15 form a partial adpack (95.3 parts).

Into each partial adpack (at 75°C) is introduced the selected amount of demulsifier and compatibility additives of this invention, together with sufficient lubricating oil to make up the balance of 100 parts of the weight of the lubricating oil concentrate. The order of mixing these additional components is varied as follows:

20 Method A. The additional required baseoil, the demulsifier of Example 1 and indicated compatibility additives are introduced into the partial adpack separately with stirring for 1.5 hours at 75°C.

Method B-1. The additional required baseoil, the demulsifier of Example 1 and compatibility additive I are first premixed together at 75°C for 1 hour, and the resulting premix is introduced into the partial adpack with mixing for an additional 1.5 hours at 75°C.

25 Method B-2. The additional required baseoil, the demulsifier of Example 1 and compatibility additive II are first premixed together at 75°C for 1 hour, and the resulting premix is introduced into the partial adpack with mixing for an additional 1.5 hours at 75°C.

Each lubricating oil concentrate is then observed for appearance, and aliquots are stored at either 54 or 66°C for an extended period to observe the appearance and to determine the onset of haze or other
30 indications of instability of the blends. The results thereby obtained are set forth in Table VI below:

TABLE VI

EX. NO.	ADDED BASEOIL (pts)(1)	DEMULSIFIER R(2) (pts)	COMPATIBILITY ADDITIVE(3)		MIXING METHOD	STORAGE STABILITY AT DAY No.:	
			I (pts)	II (pts)		54°C	66°C
19	2.9	0.3	0.5	1.0	A	haze at 61	haze at 47
20	2.4	0.3	1.0	1.0	A	haze at 26	haze at 19
21	1.9	0.3	1.5	1.0	A	haze at 19	haze at 12
22	2.9	0.3	0.5	1.0	B-2	OK at 96	OK at 96
23	1.9	0.3	1.5	1.0	B-2	haze at 26	haze at 26
24	1.9	0.3	1.5	1.0	B-1	haze at 26	haze at 26

NOTES:

(1) S150 N lubricating oil.

(2) As in Example 1: propoxylated adduct of polypropylene glycol and diglycidyl ether of bis-phenol A.

50 (3) I = glycerol monooleate; II = Diethylene glycol ester of linoleic acid dimer.

The above data illustrate the improved storage stability achieved by the premixing of the demulsifiers and compatibility additives of this invention prior to contacting the demulsifier with the remaining components of the additive package, as compared to the use of equivalent amounts of the demulsifier and compatibility additive without such premixing. The storage stability achieved by the premixing of the demulsifier with the linoleic acid dimer glycol ester additive in Example 22 (compared to the results achieved in Example 19 without such premixing) is particularly surprising in view of the art's recognition of the instability problems heretofore observed in use of such esters as friction modifiers as discussed above.

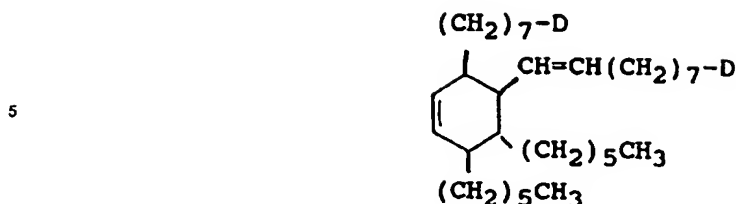
Increased storage stability also resulted from the premixing of the demulsifier with a higher concentration of the linoleic acid dimer glycol ester additive in Example 23 and by premixing the same higher concentration of the glycerol monooleate additive in Example 24 compared to the results achieved in Example 21 without any such premixing.

5

Claims

1. An oil soluble mixture useful as an oil additive comprising:
 - (A) a lubricating oil ashless additive comprising
 - (1) ashless dispersants selected from: (i) oil soluble amine salts, amides, imides, oxazolines and esters, or mixtures thereof, of long chain hydrocarbon-substituted mono and dicarboxylic acid material, i.e. acid, anhydride or ester; (ii) long chain aliphatic hydrocarbon group having a polyamine attached directly thereto; and (iii) Mannich condensation products formed by condensing about a molar proportion of long chain hydrocarbon-substituted phenol with 1 to 2.5 moles of formaldehyde and 0.5 to 2 moles of polyalkylene polyamine; wherein said long chain hydrocarbon group in (i), (ii) or (iii) is a polymer of a C₂ to C₁₀ monoolefin, said polymer having a number average molecular weight of at least 900;
 - (2) polymeric viscosity index improver dispersants selected from: (i) polymers comprised of C₄ to C₂₄ unsaturated esters of vinyl alcohol or C₃ to C₁₀ unsaturated mono- or dicarboxylic acid with unsaturated nitrogen containing monomers having 4 to 20 carbons; (ii) polymers of C₂ to C₂₀ olefin with unsaturated C₃ to C₁₀ mono- or dicarboxylic acid neutralized with amine, hydroxy amine or alcohols; and (iii) polymers of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting C₄ to C₂₀ unsaturated nitrogen containing monomers thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting said carboxylic acid groups with amine, hydroxy amine or alcohol; and mixtures of (A)(1) and (A)(2); and
 - (B) a demulsifier additive, characterised in that said demulsifier additive (B) comprises the reaction product of
 - (i) alkylene oxide having from 2 to 10 carbon atoms, and
 - (ii) an adduct obtained by reacting a polyhydric alcohol with a bis-epoxide containing at least two oxirane rings connected by a C₁ to C₁₀₀ hydrocarbon moiety which optionally contains (a) one or more of alkyl groups, tertiary amino groups and halogens as substituents thereon and/or (b) one or more oxygen atoms, sulfur atoms, carboxy groups, sulfonyl groups, sulfinyl groups, ketone groups, oxirane rings and nitro groups in the carbon chain thereof separated from the carbon atom of the oxirane ring by at least one intervening carbon atom, and wherein said demulsifier contains at least 40 wt.% of oxyalkylene units derived from said alkylene oxides of 3 or more carbon atoms.
2. The oil soluble mixture according to claim 1 wherein said bis-epoxide comprises diglycidyl ether of bis-phenol A.
3. The oil soluble mixture according to claim 1 or claim 2 wherein said alkylene oxide component (i) of said demulsifier additive is propylene oxide.
4. The oil soluble mixture according to claim 3 wherein said demulsifier additive comprises oxyalkylation units derived from butylene oxide.
5. The oil soluble mixture according to any of claims 1 to 4 wherein said polyhydric alcohol comprises polyoxyalkylene glycol.
6. The oil soluble mixture according to claim 5 wherein said polyoxyalkylene glycol has a number average molecular weight of from 1,000 to 10,000.
7. The oil soluble mixture according to claim 6 wherein said polyoxyalkylene glycol comprises polypropylene glycol.
8. The oil soluble mixture according to claim 7 wherein said polypropylene glycol has a number average molecular weight of from 2,000 to 8,000.

9. The oil soluble mixture according to any of claims 1 to 8 wherein said ashless additive comprises the reaction product of (a) a hydrocarbyl substituted C_4 to C_{10} monounsaturated dicarboxylic acid material formed by reacting an olefin polymer of C_2 to C_{10} monoolefin having a number average molecular weight of at least 900 and a C_4 to C_{10} monounsaturated acid material having an average of at least 0.8 dicarboxylic acid producing moieties per molecule of said olefin polymer present in the reaction mixture used to form said acid material, and (b) a nucleophilic reactant selected from the group consisting of amines, alcohols, amino-alcohols and mixtures thereof.
10. The oil soluble mixture according to claim 9, wherein said nucleophilic reactant comprises a polyalkylenepolyamine wherein said alkylene groups contain 2 to 40 carbons and said polyalkylenepolyamine contains from 2 to about 9 nitrogen atoms per molecule.
11. The oil soluble mixture according to claim 10, wherein said olefin polymer comprises polyisobutylene having a number average molecular weight of from 1,500 to 3,000, and wherein said monounsaturated acid material comprises maleic anhydride.
12. The oil soluble mixture according to any of claims 1 to 11, wherein said oil soluble mixture additionally contains at least one metal detergent additive (D) comprising at least one magnesium, calcium or barium salt of a material selected from the group consisting of sulfonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates and naphthenates.
13. The oil soluble mixture according to any of claims 1 to 12 which additionally contains from 0.1 to 5 parts by weight of (B) of at least one compatibility additive (C) comprising an ester or hydroxyamide derivative of a mono- or polycarboxylic acid having a total of from 24 to 90 carbon atoms and at least about 1 carboxylic acid group per molecule, with a mono-, di- or trihydric alcohol.
14. The oil soluble mixture according to claim 13 wherein said compatibility additive comprises a glycol ester having from 2 to 3 carboxylic acid groups per molecule.
15. The oil soluble mixture according to claim 14 wherein said compatibility additive comprises at least one partial ester or diester of the formulas:
- $$\text{HO-J'-OOC-J-COOH, or}$$
- $$\text{HO-J'-OOC-J-COOJ''OH}$$
- wherein J is the hydrocarbon radical of an aliphatic saturated or unsaturated polycarboxylic acid having a total of from 24 to 90 carbon atoms and from 2 to 3 carboxylic acid groups per molecule with at least 9 carbon atoms between the carboxylic acid groups, J' and J'' are the same or different and each comprises the hydrocarbon radical of an alkane diol or an oxy-alkylene radical.
16. The oil soluble mixture according to any of claims 13 to 15 wherein said compatibility additive is employed in an amount of from 0.5 to 1.5 parts by weight based upon the overall weight of said demulsifier additive (B) in said oil soluble mixture.
17. The oil soluble mixture according to claim 13 wherein said compatibility additive comprises at least one ester of a substituted cyclohexene dicarboxylic acid formed by a Diels-Alder thermal condensation of C_{18} - C_{22} unsaturated fatty acids.
18. The oil soluble mixture according to claim 17 wherein said unsaturated fatty acid comprises oleic acid, linoleic acid, or a mixture thereof.
19. The oil soluble mixture according to claim 18 wherein said compatibility additive comprises an ester of the formula:



wherein D is



x' is an integer of from 1 to 100.

- 20 20. A lubricating-oil additive concentrate containing from 10 to 80 wt.% of an oil soluble mixture according to any preceding claim dissolved in a hydrocarbon oil.
21. A concentrate according to claim 20 comprising:
 from 3 to 45 wt.% of a said ashless dispersant (A)(1)
 from 0.01 to 3 wt.% of a said demulsifier additive (B)
 from 0.0005 to 2 wt.% of a said compatibility additive (C), and
 from 2 to 45 wt.% of a said metal detergent additive (D).
22. A process for forming a concentrate according to claim 20 or claim 21 wherein a said ashless dispersant (A)(1) and a said metal detergent component (D) are pre-mixed at 70 to 130 °C, and wherein a said demulsifier additive (B) and a said compatibility additive (C) are separately mixed, and the separate mixtures are then mixed together.
23. A lubricant composition comprising a concentrate according to claim 20 or 21 or obtainable by the process of claim 22 diluted with 3 to 100 parts by weight (per part by weight of concentrate) of lubricating oil.

Patentansprüche

- 40 1. Öllösliche Mischung, die als Öl-Additiv brauchbar ist und (A) aschefreies Schmieröladditiv, das
- (1) aschefreie Dispergiermittel ausgewählt aus (i) öllöslichen Aminsäuren, Amidinen, Imiden, Oxazolinen und Estern oder Mischungen hiervon aus mit langkettigem Kohlenwasserstoff substituierten Mono- und Dicarbonsäurematerial, d. h. Säure, Anhydrid oder Ester, (ii) einer langkettigen aliphatischen Kohlenwasserstoffgruppe mit einem direkt daran gebundenen Polyamin, und (iii) Mannich-Kondensationsprodukten, die durch Kondensieren von etwa einem molaren Anteil mit langkettigem Kohlenwasserstoff substituiertem Phenol mit 1 bis 2,5 Mol Formaldehyd und 0,2 bis 2 Mol Polyalkylenpolyamin gebildet worden sind, wobei die langkettige Kohlenwasserstoffgruppe in (i), (ii) oder (iii) ein Polymer eines C_2 - bis C_{10} -Monoolefins ist und dieses Polymer ein durchschnittliches Molekulargewicht (Zahlenmittel) von mindestens 900 aufweist,
- (2) polymeres Viskositätsindexverbesserer-Dispergiermittel ausgewählt aus (i) Polymeren, die aus ungesättigten C_4 - bis C_{24} -Ethern von Vinylalkohol oder ungesättigter C_3 - bis C_{10} -Mono- oder Dicarbonsäure und ungesättigten stickstoffhaltigen Monomeren mit 4 bis 20 Kohlenstoffatomen zusammengesetzt sind, (ii) Polymeren aus C_2 - bis C_{20} -Olefin und ungesättigter C_3 - bis C_{10} -Mono- oder -Dicarbonsäure, die mit Amin, Hydroxyamin oder Alkoholen neutralisiert ist, und (iii) Polymeren aus Ethylen und einem C_3 - bis C_{20} -Olefin, die weiter umgesetzt wurden, indem ungesättigte stickstoffhaltige C_4 - bis C_{20} -Monomere darauf gepfropft wurden oder indem eine ungesättigte Säure auf das Polymergrundgerüst gepfropft wurde und dann die Carbonsäuregrup-

pen mit Amin, Hydroxyamin oder Alkohol umgesetzt wurden, und Mischungen aus (A)(1) und (A)-(2) umfaßt, und

(B) Demulgator-Additiv umfaßt,

dadurch gekennzeichnet, daß das Demulgator-Additiv (B) das Reaktionsprodukt aus

- 5 (i) Alkylenoxid mit 2 bis 10 Kohlenstoffatomen und
- (ii) einem Addukt umfaßt, das durch Umsetzung von mehrwertigem Alkohol mit Bis-epoxid erhalten wurde, das mindestens zwei durch eine C₁- bis C₁₀₀-Kohlenwasserstoffgruppe verbundene Oxiranringe enthält, wobei die Kohlenwasserstoffgruppe gegebenenfalls (a) eine oder mehrere Alkylgruppen, tertiäre Aminogruppen und Halogene als Substituenten enthält und/oder ein oder mehrere Sauerstoffatome, Schwefelatome, Carboxygruppen, Sulfonylgruppen, Sulfinylgruppen, Ketongruppen, Oxiranringe und Nitrogruppen in der Kohlenstoffkette enthält, die von dem Kohlenstoffatom des Oxiranrings durch mindestens ein dazwischenliegendes Kohlenstoffatom getrennt sind, und der Demulgator mindestens 40 Gew.% von den von den Alkylenoxiden mit 3 oder mehr Kohlenstoffatomen abgeleiteten Oxyalkyleneinheiten enthält.

15 2. Öllösliche Mischung nach Anspruch 1, bei der das Bis-epoxid den Diglycidylether von Bisphenol A umfaßt.

20 3. Öllösliche Mischung nach Anspruch 1 oder Anspruch 2, bei der die Alkylenoxidkomponente (i) des Demulgator-Additivs Propylenoxid ist.

4. Öllösliche Mischung nach Anspruch 3, bei der das Demulgator-Additiv von Butylenoxid abgeleitete Oxyalkylierungseinheiten aufweist.

25 5. Öllösliche Mischung nach einem der Ansprüche 1 bis 4, bei der der mehrwertige Alkohol Polyoxyalkylenglykol umfaßt.

6. Öllösliche Mischung nach Anspruch 5, bei der das Polyoxyalkylenglykol ein durchschnittliches Molekulargewicht (Zahlenmittel) von 1 000 bis 10 000 aufweist.

30 7. Öllösliche Mischung nach Anspruch 6, bei der das Polyoxyalkylenglykol Polypropylenglykol umfaßt.

8. Öllösliche Mischung nach Anspruch 7, bei der das Polypropylenglykol ein durchschnittliches Molekulargewicht (Zahlenmittel) von 2 000 bis 8 000 aufweist.

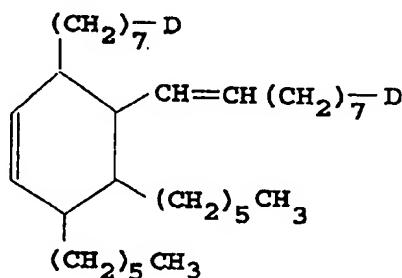
35 9. Öllösliche Mischung nach einem der Ansprüche 1 bis 8, bei der das aschefreie Additiv das Reaktionsprodukt aus (a) kohlenwasserstoffsubstituiertem, einfach ungesättigten C₄- bis C₁₀-Dicarbonsäurematerial, das durch Umsetzen eines Olefinpolymers aus C₂- bis C₁₀-Monoolefin mit einem durchschnittlichen Molekulargewicht (Zahlenmittel) von mindestens 900 mit einem einfach ungesättigten C₄- bis C₁₀-Säurematerial gebildet wird, das mindestens durchschnittlich 0,8 Dicarbonsäure produzierenden Gruppen pro Molekül des in der Reaktionsmischung zur Bildung des Säurematerials vorhandenen Olefinpolymers aufweist, und (b) einem nukleophilen Reaktanten ausgewählt aus der Gruppe bestehend aus Aminen, Alkoholen, Aminoalkoholen und Mischungen davon umfaßt.

45 10. Öllösliche Reaktionsmischung nach Anspruch 9, bei der der nukleophile Reaktant Polyalkylenpolyamin umfaßt, bei dem die Alkylengruppen 2 bis 40 Kohlenstoffatome enthalten und das Polyalkylenpolyamin 2 bis etwa 9 Stickstoffatome pro Molekül enthält.

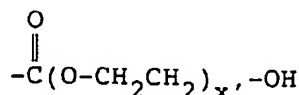
50 11. Öllösliche Mischung nach Anspruch 10, bei der das Olefinpolymer Polyisobutylen mit einem durchschnittlichen Molekulargewicht (Zahlenmittel) von 1 500 bis 3 000 und das einfach ungesättigte Säurematerial Maleinsäureanhydrid umfaßt.

55 12. Öllösliche Mischung nach einem der Ansprüche 1 bis 11, bei der die öllösliche Mischung zusätzlich mindestens ein Metaldetergens-Additiv (D) enthält, das mindestens ein Magnesium-, Calcium- oder Bariumsalz eines Materials ausgewählt aus der Gruppe bestehend aus Sulfonsäuren, Alkylphenolen, sulfurierten Alkylphenolen, sulfurierten Alkylphenolen, Alkylsalicylaten und Naphthenaten umfaßt.

13. Öllösliche Mischung nach einem der Ansprüche 1 bis 12, die zusätzlich 0,1 bis 5 Gewichtsteile von mindestens einem Verträglichkeitsadditiv (C) bezogen auf (B) enthält, wobei (C) ein Ester- oder Hydroxyamid-Derivat einer Mono- oder Polycarbonsäure mit insgesamt 24 bis 90 Kohlenstoffatomen und mindestens etwa 1 Carbonsäuregruppe pro Molekül mit einem ein-, zwei- oder dreiwertigen Alkohol ist.
14. Öllösliche Mischung nach Anspruch 13, bei der das Verträglichkeitsadditiv einen Glykolester mit 2 bis 3 Carbonsäuregruppen pro Molekül umfaßt.
15. Öllösliche Mischung nach Anspruch 14, bei der das Verträglichkeitsadditiv mindestens einen Partialester oder Diester mit den Formeln
- $$\text{HO-J'-OOC-J-COOH oder}$$
- $$\text{HO-J'-OOC-J-COOJ''-OH}$$
- umfaßt, in denen J der Kohlenwasserstoffrest einer aliphatischen, gesättigten oder ungesättigten Polycarbonsäure mit insgesamt 24 bis 90 Kohlenstoffatomen, 2 bis 3 Carbonsäuregruppen pro Molekül und mindestens 9 Kohlenstoffatomen zwischen den Carbonsäuregruppen ist, und J' und J'' gleich oder unterschiedlich sind und jeweils den Kohlenwasserstoffrest eines Alkandiolis oder einen Oxyalkylenrest umfassen.
16. Öllösliche Mischung nach einem der Ansprüche 13 bis 15, bei der das Verträglichkeitsadditiv in einer Menge von 0,5 bis 1,5 Gewichtsteilen, bezogen auf das Gesamtgewicht des Demulgator-Additivs (B) in der öllöslichen Mischung, verwendet wird.
17. Öllösliche Mischung nach Anspruch 13, bei der das Verträglichkeitsadditiv mindestens einen Ester einer substituierten Cyclohexendicarbonsäure umfaßt, die durch eine thermische Diels-Alder-Kondensation von ungesättigten C₁₈- bis C₂₂-Fettsäuren gebildet worden ist.
18. Öllösliche Mischung nach Anspruch 17, bei der die ungesättigte Fettsäure Ölsäure, Linolsäure oder eine Mischung davon umfaßt.
19. Öllösliche Mischung nach Anspruch 18, bei der das Verträglichkeitsadditiv einen Ester mit der Formel



umfaßt, in der D



und x' eine ganze Zahl von 1 bis 100 ist.

20. Schmieröladditivkonzentrat, das 10 bis 80 Gew.% öllösliche Mischung gemäß einem der vorhergehenden Ansprüche in einem Kohlenwasserstofföl aufgelöst enthält.

21. Konzentrat nach Anspruch 20, das
 3 bis 45 Gew.% des aschfreien Dispergiermittels (A)(1),
 0,01 bis 3 Gew.% des Demulgator-Additivs (B),
 0,0005 bis 2 Gew.% des Verträglichkeitsadditivs (C) und
 2 bis 45 Gew.% des Metaldetergens-Additivs (D) umfaßt.
22. Verfahren zur Bildung eines Konzentrats nach Anspruch 20 oder 21, bei dem das aschefreie Dispergiermittel (A)(1) und die Metaldetergenskomponente (D) bei 70 bis 130°C vorgemischt werden und das Demulgator-Additiv (B) und das Verträglichkeitsadditiv (C) separat gemischt werden, und die separaten Mischungen dann zusammengemischt werden.
23. Schmierstoffzusammensetzung, die ein Konzentrat nach Anspruch 20 oder 21 oder gemäß dem Verfahren nach Anspruch 22 erhältlich umfaßt, welches mit 3 bis 100 Gewichtsteilen (pro Gewichtsteil Konzentrat) Schmieröl verdünnt ist.

Revendications

1. Mélange soluble dans l'huile, utile comme additif d'huile, comprenant :
- (A) un additif sans cendre pour huile lubrifiante, comprenant
- (1) des dispersants sans cendre choisis entre : (i) des sels d'amines, des amides, des imides, des oxazolines et des esters solubles dans l'huile, ou leurs mélanges, d'une matière du type acide, c'est-à-dire un acide, un anhydride ou un ester, mono- ou dicarboxylique à substituant hydrocarboné à chaîne longue ; (ii) un groupe hydrocarboné aliphatique à chaîne longue possédant une polyamine fixée directement à ce groupe ; et (iii) des produits de condensation de Mannich formés par condensation d'approximativement une proportion molaire d'un phénol à substituant hydrocarboné à chaîne longue avec 1 à 2,5 moles de formaldéhyde et 0,5 à 2 moles d'une polyalkylènepolyamine ; ledit groupe hydrocarboné à chaîne longue dans (i), (ii) ou (iii) étant un polymère d'une mono-oléfine en C₂ à C₁₀, ledit polymère ayant une moyenne numérique du poids moléculaire d'au moins 900 ;
- (2) des dispersants-améliorants d'indice de viscosité polymériques choisis entre : (i) des polymères constitués d'esters insaturés en C₄ à C₂₄ d'alcool vinylique ou d'un acide mono- ou dicarboxylique insaturé en C₃ à C₁₀ avec des monomères azotés insaturés ayant 4 à 20 atomes de carbone ; (ii) des polymères d'une oléfine en C₂ à C₂₀ avec un acide mono- ou dicarboxylique insaturé en C₃ à C₁₀ neutralisé avec une amine, une hydroxyamine ou des alcools ; et (iii) des polymères d'éthylène avec une oléfine en C₃ à C₂₀, soumis à une réaction supplémentaire par greffage de monomères azotés insaturés en C₄ à C₂₀ sur ces polymères ou par greffage d'un acide insaturé sur le squelette du polymère, puis réaction desdits groupes acide carboxylique avec une amine, une hydroxyamine ou un alcool ; et des mélanges de (A)(1) et (A)(2) ; et
- (B) un additif désémulsionnant,
- caractérisé en ce que ledit additif désémulsionnant (B) comprend le produit de réaction
- (i) d'un oxyde d'alkylène ayant 2 à 10 atomes de carbone, et
- (ii) d'un produit d'addition obtenu par réaction d'un alcool polyhydroxylique avec un bis-époxyde contenant au moins deux noyaux oxiranne connectés par un groupement hydrocarboné en C₁ à C₁₀₀ qui contient facultativement (a) un ou plusieurs groupes alkyle, groupes amino tertiaires ou halogènes comme substituants sur ce groupement, et/ou (b) un ou plusieurs atomes d'oxygène, atomes de soufre, groupes carboxy, groupes sulfonyle, groupes sulfinyle, groupes cétone, noyaux oxiranne et groupes nitro dans sa chaîne carbonée séparés de l'atome de carbone du noyau oxiranne par au moins un atome de carbone intermédiaire, ledit désémulsionnant contenant au moins 40 % en poids de motifs oxyalkylène dérivés desdits oxydes d'alkylène ayant 3 ou plus de 3 atomes de carbone.
2. Mélange soluble dans l'huile suivant la revendication 1, dans lequel le bis-époxyde comprend un éther de diglycidyle de bis-phénol A.
3. Mélange soluble dans l'huile suivant la revendication 1 ou la revendication 2, dans lequel le constituant (i) du type oxyde d'alkylène de l'additif désémulsionnant est l'oxyde de propylène.

4. Mélange soluble dans l'huile suivant la revendication 3, dans lequel l'additif désémulsionnant comprend des motifs oxyalkylène dérivés de l'oxyde de butylène.
5. Mélange soluble dans l'huile suivant l'une quelconque des revendications 1 à 4, dans lequel l'alcool polyhydroxylique comprend un polyoxyalkylène-glycol.
6. Mélange soluble dans l'huile suivant la revendication 5, dans lequel le polyoxyalkylène-glycol possède une moyenne numérique du poids moléculaire de 1000 à 10 000.
7. Mélange soluble dans l'huile suivant la revendication 6, dans lequel le polyoxyalkylène-glycol comprend le polypropylène-glycol.
8. Mélange soluble dans l'huile suivant la revendication 7, dans lequel le polypropylène-glycol possède une moyenne numérique du poids moléculaire de 2000 à 8000.
9. Mélange soluble dans l'huile suivant l'une quelconque des revendications 1 à 8, dans lequel l'additif sans cendre comprend le produit de réaction (a) d'une matière du type acide dicarboxylique mono-insaturé en C₄ à C₁₀ à substituant hydrocarbyle formée par réaction d'un polymère oléfinique d'une mono-oléfine en C₂ à C₁₀ ayant une moyenne numérique du poids moléculaire d'au moins 900 et d'une matière du type acide mono-insaturé en C₄ à C₁₀ ayant une moyenne d'au moins 0,8 groupement producteur d'acide dicarboxylique par molécule dudit polymère oléfinique présente dans le mélange réactionnel utilisé pour former ladite matière acide, et (b) d'un corps réactionnel nucléophile choisi dans le groupe consistant en amines, alcools, amino-alcools et leurs mélanges.
10. Mélange soluble dans l'huile suivant la revendication 9, dans lequel le corps réactionnel nucléophile comprend une polyalkylènenéopolyamine dans laquelle les groupes alkylène contiennent 2 à 40 atomes de carbone, ladite polyalkylènenéopolyamine contenant 2 à environ 9 atomes d'azote par molécule.
11. Mélange soluble dans l'huile suivant la revendication 10, dans lequel le polymère oléfinique comprend un polyisobutylène ayant une moyenne numérique du poids moléculaire de 1500 à 3000, et dans lequel la matière du type acide mono-insaturé comprend l'anhydride maléique.
12. Mélange soluble dans l'huile suivant l'une quelconque des revendications 1 à 11, qui contient en outre au moins un additif détergent métallique (D) comprenant au moins un sel de magnésium, de calcium ou de baryum d'une matière choisie dans le groupe consistant en acides sulfoniques, alkylphénols, alkylphénols sulfurés, salicylates et naphthénates d'alkyle.
13. Mélange soluble dans l'huile suivant l'une quelconque des revendications 1 à 12, qui contient en outre 0,1 à 5 parties en poids de l'additif (B) d'au moins un additif de compatibilité (C) comprenant un ester ou dérivé d'hydroxyamide d'un acide mono- ou polycarboxylique ayant un nombre total de 24 à 90 atomes de carbone et au moins environ un groupe acide carboxylique par molécule avec un alcool mono-, di- ou trihydroxylique.
14. Mélange soluble dans l'huile suivant la revendication 13, dans lequel l'additif de compatibilité comprend un ester de glycol ayant 2 ou 3 groupes acide carboxylique par molécule.
15. Mélange soluble dans l'huile suivant la revendication 14, dans lequel l'additif de compatibilité comprend au moins un ester ou diester partiel de formule :
$$\text{HO-J'-OOC-J-COOH ou}$$
$$\text{HO-J'-OOC-J-COOJ''-OH}$$

dans laquelle J représente le radical hydrocarboné d'un acide polycarboxylique aliphatique saturé ou insaturé ayant un nombre total de 24 à 90 atomes de carbone et 2 ou 3 groupes acide carboxylique par molécule avec au moins 9 atomes de carbone entre les groupes acide carboxylique, J' et J'' sont identiques ou différents et comprennent chacun le radical hydrocarboné d'un alcane-diol ou d'un radical oxyalkylène.

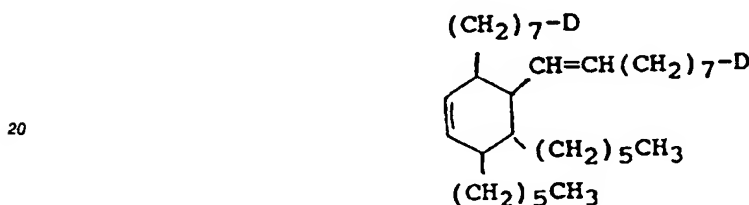
16. Mélange soluble dans l'huile suivant l'une quelconque des revendications 13 à 15, dans lequel l'additif de compatibilité est utilisé en une quantité de 0,5 à 1,5 partie en poids sur la base du poids total de l'additif désémulsionnant (B) dans le mélange soluble dans l'huile.

5 17. Mélange soluble dans l'huile suivant la revendication 13, dans lequel l'additif de compatibilité comprend au moins un ester d'un acide cyclohexènedicarboxylique substitué formé par une condensation thermique de Diels-Alder d'acides gras insaturés en C₁₈ à C₂₂.

10 18. Mélange soluble dans l'huile suivant la revendication 17, dans lequel l'acide gras insaturé comprend l'acide oléique, l'acide linoléique ou un de leurs mélanges.

19. Mélange soluble dans l'huile suivant la revendication 18, dans lequel l'additif de compatibilité comprend un ester de formule :

15



25 dans laquelle D représente un groupe



x' représente un nombre entier de 1 à 100.

35 20. Concentré d'additif pour huile lubrifiante, contenant 10 à 80 % en poids d'un mélange soluble dans l'huile suivant l'une quelconque des revendications précédentes, dissous dans une huile hydrocarbonnée.

21. Concentré suivant la revendication 20, comprenant :
 3 à 45 % en poids d'un des dispersants sans cendre (A) (1)
 0,01 à 3 % en poids d'un des additifs désémulsionnants (B)
 0,0005 à 2 % en poids d'un des additifs de compatibilité (C), et
 2 à 45 % en poids d'un des additifs détergents métalliques (D).

45 22. Procédé pour former un concentré suivant la revendication 20 ou la revendication 21, dans lequel un des dispersants sans cendre (A) (1) et un des constituants détergents métalliques (D) sont mélangés préalablement à une température de 70 à 130 °C, et dans lequel un des additifs désémulsionnants (B) et un des additifs de compatibilité (C) sont mélangés séparément, et les mélanges distincts sont ensuite mélangés l'un à l'autre.

50 23. Composition de lubrifiant comprenant un concentré suivant la revendication 20 ou 21 ou pouvant être obtenue par le procédé suivant la revendication 22, diluée avec 3 à 100 parties en poids (par partie en poids de concentré) d'une huile lubrifiante.

55